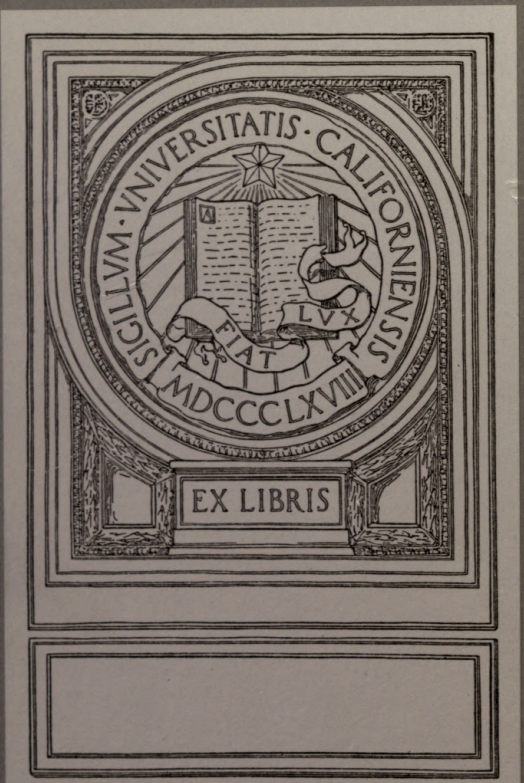
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CHEMISTRY IN DAILY LIFE

CHEMISTRY IN DAILY LIFE

POPULAR LECTURES

BY

DR. LASSAR-COHN

Professor in the University of Königsberg; Author of "A Laboratory Manual of Organic Chemistry," etc.

TRANSLATED BY

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With Twenty-four Woodcuts in the Text

FIFTH EDITION, REVISED AND AUGMENTED

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PREFACE

TO THE FIFTH EDITION

PROFESSOR LASSAR-COHN'S book has been translated into thirteen languages; Czech, English, Finnish, French, Hebrew, Hungarian, Italian, Polish, Portuguese, Russian, Servian, Spanish, and Swedish. An edition has been prepared for the use of German blind people. An unauthorised edition has been published in New York, with English notes, for use as a German reading book in English schools.

Very considerable changes in the text, both omissions and additions, have been made by the Author in preparing the seventh German edition. Most of these changes and additions have been put into their proper places in this the fifth English edition.

M. M. P. M.

FARNHAM, *April* 1913.

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PREFACE

TO THE THIRD EDITION

THE Author has been so good as to supply a few additions, designed by him to make the book of more general interest, and to bring it up to date; these have been put into their proper places in the text. He has also allowed me to see his corrected proofs for the fourth German edition.

I have ventured to make a few small changes; these have been submitted to Professor Lassar-Cohn, and approved by him.

M. M. P. M.

CAMBRIDGE, *November* 1904.

PREFACE

TO THE FIRST EDITION

THIS book, which now appears in English, embodies the substance of a course of lectures delivered by Dr. Lassar-Cohn, Professor of Chemistry in the University of Königsberg, to a society in that town modelled on the celebrated *Humboldt Academy* of Berlin.

These lectures, and the publication of them in book form, caused quite a stir in German circles. And it is in the hope that they will prove at once interesting, instructive, and suggestive to English readers that I have prepared a translation at the request of the publishers.

That the lectures cover a great variety of topics will be evident from a glance at the *Table of Contents*. The method of treatment is eminently human and suggestive. The author shows that chemical phenomena are intimately bound up with our daily lives, and that whether we are conscious of it or not we are constantly carrying on chemical operations. He also brings home to us how chemical considerations play their part in those speculations regarding the physical universe that are suggested by each fresh discovery made by science.

Vague notions circulate in men's minds concerning

chemistry. Some think the chemist is a man who compounds drugs and mixes pills; and others look on him as an astrologer of the modern sort. This book shows that the chemist is in a sense both of these, and much more than both; it causes the careful reader to realise the permeating nature of chemical knowledge, and it teaches him that chemistry is emphatically the most human, and for that reason the most fascinating, of the sciences.

The book can be followed intelligently by any reader who gives it a little care; no special technical knowledge is required.

The translation has been made from a copy of the original book kindly lent by the Author containing Dr. Lassar-Cohn's corrections and additions.

The very few additions made by the Translator are inclosed in square brackets.

M. M. P. M.

CAMBRIDGE, *May* 1896.

CONTENTS

LECTURE I

PAGE

Breathing—Physics and chemistry—The weight of the air—Analysis of air—Argon—Difference between inspired and expired breath—Maintenance of the warmth of the body—Combustion—Oxidation—Matches—Yellow and red phosphorus . . . 1

LECTURE II

Nature of flame: (1) Candles—Composition of fats—Oils—Petroleum—Hydrocarbons—The elements—Tetravalency of the atom of carbon—Chemical formulæ—The atom and the molecule—Distillation—Petroleum ether—Vaseline—Paraffin—Ozone—Manufacture of coal-gas—Nature of flame: (2) Cooking by gas—Incandescent gaslights—Electric furnace—Acetylene 16

LECTURE III

Food of plants—Manuring—Fallow land—Artificial manures—Bones—Superphosphates—Potash salts—Manuring with nitrogen—Bases, acids, and salts—Mother-liquor—Food of men and animals—Experiments on digestion—Albuminoids—Fats—Carbohydrates—Milk and its coagulation—Cheese—Soxhlet's extraction apparatus—Fibrin—Serum—Artificial fodder—Gelatin 36

LECTURE IV

PAGE

Mixed diet—Butter—Margarine—Starch—The sugars—Ripening of fruits—The diet of diabetic patients—Fruit-sugar—Bonbons—Burnt sugar as a colouring material—Cane sugar—Saccharin—The absorption of food—Common salt—Iron—Importance of cooking—Soups—Bread making—Boiling potatoes . . 63

LECTURE V

Quantity of food that must be consumed, and nutritive values of the chief foods—Fermentation—Wine—Cider and perry—Champagne—Mead—Koumiss—Beer—Malt—Spirits—Dry yeast [German yeast]—Brandy—Potato spirit—Vinasse—Spirit refining—Absolute alcohol—Methylated alcohol—Liqueurs . 89

LECTURE VI

Wine vinegar—Wood vinegar—Glacial acetic acid—Wood spirit—Acetone—Gunpowder—Greek fire—Fulminating mercury—Guncotton—Dynamite—Collodion—Blasting gelatin—Cordite—Chlorate explosives—Wool—Cotton—Silk—Artificial wool [Shoddy]—Carbonising—Mercerised cotton—Artificial silk . 116

LECTURE VII

Tanning—Leather—Removing hair from hides and softening them—Tanning materials—Barks—Quebracho bark—Sumac—Tanning extracts—Sole leather—Alum tanning—Glove leather—Furriery—Iron and chrome leather—Chamois leather—Wash leather—Parchment—Bleaching on meadows—Blueing washed linen—Bleaching by chlorine—Bleaching powder—Antichlors—*Eau de Javelle*—Sulphurous acid—*Persil*—Dyeing—Mordants—Lakes—Substantive colours—Coal tar colours—Indigo—Alizarin—Colouring pastes—Colouring extracts from woods—Log-wood—Calico printing 136

LECTURE VIII

PAGE

Oil-painting—Drying and non-drying oils—Linseed oil—Varnishes —Inks—Cellulose—Paper—Sizing paper—Straw boiling—Esparto grass boiling—Soda cellulose—Sulphite cellulose—Silvalin 159

LECTURE IX

Burnt lime—Potash—Soda by Leblanc's process—Sulphuric acid—Sulphate of soda—Nitric acid—Bleaching powder—Soda crystals—Ammonia soda process—Ashes of molasses—Ashes from the washings of wool—Soap—Caustic alkali—Caustic soda—Soft soaps—Loaded soaps—Curd soaps—Hard and soft waters—Plasters 176

LECTURE X

Glass—Glass mirrors—Potash and soda glass—Quartz glass—*Strass* —Artificial precious stones—Ruby glass—Milk glass—Clay—Bricks — Mortars — Lime sandstone bricks — Cements — Glazing—Pottery—Stoneware—Majolica ware—Porcelain—Photography—Lunar caustic—Chloride, bromide, and iodide of silver—Daguerreotypes—Development of the negative—Talbotypes—Albumen methods—Wet collodion processes—Dry silver bromide emulsion plates—Platinotypes—Photography of the spectrum—Red light—Orthochromatic plates—Colour photography—Chrome-gelatin—Pigment printing—Röntgen rays—Radio-activity—Radium 199

LECTURE XI

Noble and base metals — Ores — Gold — Platinum—Potassium cyanide — Silver — Relations of value between gold and silver—Bimetallism—Gold currency—Reduction of metallic oxides — Roasting sulphur compounds — Pig iron — Steel—Wrought iron — Blast furnaces —Slags—Coke — Puddling—

PAGE

Rolled iron—Railways—Cementation steel—Cast steel—Bessemer steel—*Spiegeleisen*—Manganese—Dephosphorising iron—Soft steel—Nickel steel—Chromium steel—Gas furnaces—Regenerative furnaces—Open flame furnaces—Zinc—Electro-deposition of metals—Potassium—Sodium—Aluminium . 241

LECTURE XII

ALLOYS: Coinage—Bronze—Patina—Brass—Tombac—Talmi gold—Nickel silver—Britannia metal—Type metal—Nickel steel—Rare metals

ALKALOIDS: Methane—Acetylene gas—Benzene—Pyridine—Coniine—Quinoline—Kairine—Antipyrin—Phenacetin—Narcotine—Chloral—Ether—Hoffman's drops—Chloroform—Antiseptics—Iodoform—Carbolic acid—Corrosive sublimate—Salicylic acid 287

INDEX 311

CHEMISTRY IN DAILY LIFE

LECTURE I

Breathing—Physics and chemistry—The weight of the air—Analysis of air—Argon—Difference between inspired and expired breath—Maintenance of the warmth of the body—Combustion—Oxidation—Matches—Yellow and red phosphorus.

IN the lectures which begin to-day I hope to convince you that a foundation of chemical knowledge is needed for understanding many occurrences of everyday life. We shall see that there are many facts which have become so familiar to us by custom that we pay scarcely any heed to them, and seldom give ourselves the trouble of thinking about the more intimate relations of them.

Let us begin by considering an action which we perform constantly—the action, namely, of breathing. We speak of the duration of our lives as the time between our first and last breaths.

At once we are faced by the question, What do we breathe, and for what purpose do we breathe? Every one knows that we breathe the air which surrounds us. But what is this air?

Here it is necessary to make a short excursion into the domain of physics, which is a branch of science that concerns itself with occurrences, such as the magnetisation of iron,

wherein no change of material composition takes place. Chemistry, on the other hand, is that part of natural knowledge whose task it is to investigate events, such, for instance, as the rusting of iron, wherein changes of material composition do take place. When a piece of iron is magnetised, it is not changed internally or externally from its former condition, except that it acquires the power of attracting other small pieces of iron ; on the other hand, when iron rusts, it is changed into a brown substance which is something quite different from iron—for instance, it is not rigid like iron, but can be rubbed to powder between the fingers.

To return to our main theme. Is the air something which has an actual material existence, or is it only existent in our imagination? For it cannot be asserted that any one possesses a sense-organ whereby he can discover the actual existence of air. We talk, indeed, of the heaviness of the air; but I fancy there is scarcely one among those present who is able to determine accurately the weight of a definite quantity of air—say, for instance, the weight in kilograms of the air in the room wherein we are assembled.

We cannot directly convince ourselves that the air is heavy. We wave our hands to and fro in the air without any apparent hindrance ; we even move our whole bodies without trouble through the air. And although these facts, and many other similar facts, seem entirely to contradict the notion that air is heavy, nevertheless every one knows to-day that air weighs something. But this is only because every one has been accustomed from his youth to hear this property of air spoken of with absolute certainty.

If we consider a little, we shall find many other well-established facts in the domain of natural science which no

one doubts, although these facts cannot be demonstrated directly. For instance, every one admits that the shape of the earth is that of a sphere, although no proof of this has yet been found that can be grasped without much difficulty by lay minds.*

We are, however, in a better position in dealing with the case before us, inasmuch as we can easily convince ourselves of the weight, and hence of the material existence, of the atmosphere. For this purpose let us carry out a simple experiment.

The flask A (fig. 1) is placed on one pan of a balance, and the beam is brought into equilibrium by placing weights on the other pan. The special things to be noticed about this flask are, that the neck has been drawn out to a fine opening, that the air has then been pumped out of the flask by means of an air-pump, and that the neck has then been sealed by melting the glass; the interior of the flask is evidently cut off from the air outside. When I now break the end of the neck of the flask by means of pliers, the pan in which the flask rests sinks, although the flask cannot have been made heavier by cutting off the end of the neck. The cause of this occurrence is that air rushes into the flask through the opened neck, and the heaviness of this air is made visible to us by the descent of the balance-pan. If we know the capacity of the flask, and if we now place weights on the

* The fact that at sea the tops of the masts of an approaching vessel are the first parts of her to be seen is often adduced as the simplest proof of the curvature of the earth's surface caused by the spherical form of the earth. Although the Greeks and Romans often observed the phenomenon in question, yet they did not draw the conclusion that the earth is spherical; but among them were many clear-headed men. The alleged proof is quite inconclusive of itself, and it came to the front only after the spherical form of the earth had been established on the basis of strictly scientific investigations.

other pan till equilibrium is re-established, we can read off directly the weight of the air which has rushed into and filled the flask. Careful experiments have shown that one litre of air weighs 1·295 grams [one cubic foot weighs 564 grains].

If air is a material thing, it must exert a pressure, because of its weight, on every object whereon it impinges. Forestalling what is to be dealt with later, we shall at once

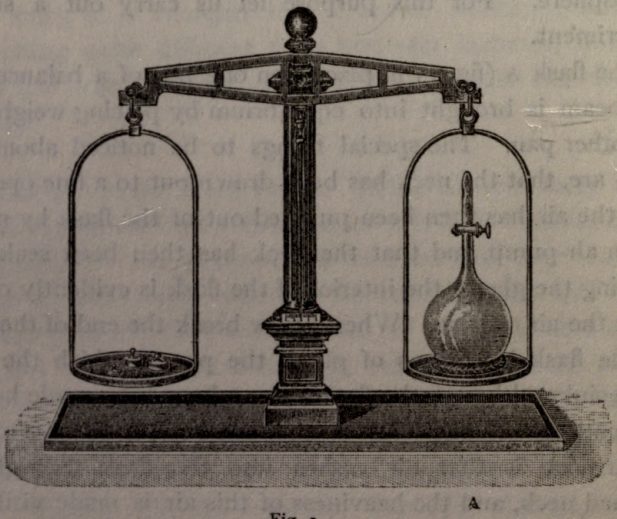


Fig. 1.

convince ourselves of the justness of this conclusion. The following simple experiment will serve our purpose. We take a flask which has been sealed after all the air has been pumped out of it, and bring the neck under water as shown in the figure (fig. 2); we then break off the end of the neck. We see the water at once rush rapidly into the flask and fill it. The reason of this is that the air outside the flask presses on the surface of the water in the vessel, and, inasmuch as there is no contrary pressure inside the flask from which the air

has been exhausted, this pressure causes the water to rush inwards through the opened neck of the flask.

Had we conducted a similar experiment, using a very long tube in place of the flask, we should have noticed that the pressure of the air would have held up the water to a height of more than 10 metres. If in place of water we use mercury, a liquid which is about 13·5 times heavier than water, the air will press this upwards to a height about 13·5 times less than that to which it forces water—that is, in round numbers, to a height of 760 millimetres [30 inches]. A column of mercury 30 inches high is in equilibrium with the pressure of the atmosphere, and as the latter increases or decreases the mercury in the tube rises or falls. For this reason we make use of such a column of mercury, under the name of *barometer* (derived from the Greek word $\beta\alpha\rho\acute{\upsilon}\varsigma$ = heavy), as a measure of the weight, or more correctly of the pressure, of the atmosphere.

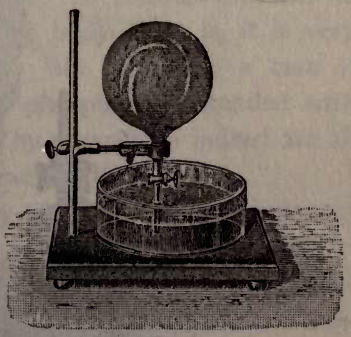


Fig. 2.

By this time we know that the air is a material substance. But now comes the question : is air a homogeneous body, or is it made up of several constituents?

It can, evidently, be no easy task to analyse—that is, to test for its constituents—something which we are unable to grasp in our hands or to see with our eyes ; and, indeed, the solution of this most ancient problem was partially gained only about a hundred years ago.

It is possible to demonstrate to you, without assuming any

chemical knowledge on your part, that air must contain at least two components—one, namely, which maintains combustion, and another which does not do this.

For this purpose we proceed as follows. By immersing a glass jar in water we cut off a definite volume of air from the rest of the atmosphere. A little piece of phosphorus is placed in a small basin which is floated on the surface of the water inside the jar (see fig. 3). I now remove the jar,

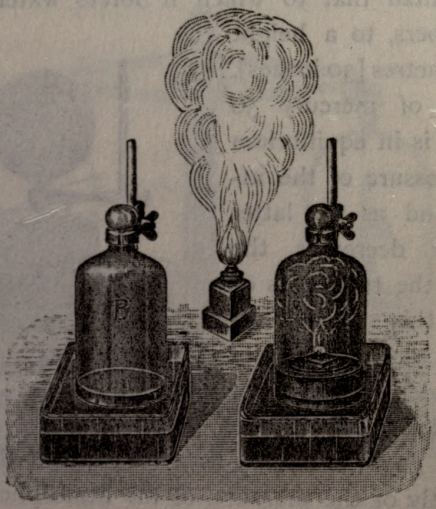


Fig. 3. Fig. 4.

ignite the phosphorus, and again place the jar over the little basin. The phosphorus continues to burn brightly for a short time, while it combines with a part of the air in the jar, and then goes out. While this is going on, the external air-pressure forces water into the jar, to take the place of the air which has been removed, and the removal of which has produced a partial vacuum in the jar, and the quantity of water so driven into the jar corresponds with the quantity of air which has combined with the phosphorus (fig. 4).

An examination of the gas left in the jar shows that it differs from the atmosphere around us in that a burning body, even a substance so combustible as phosphorus, goes out when brought into this gas; and in many other respects the gas is found to be very indifferent—that is, it shows scarcely any inclination to combine with other substances, and so to form new bodies. This gas is called *nitrogen*. Living things die in it.

The other part of the air which combined with phosphorus in the experiment just described is called *oxygen*, from the Greek word ὀξύς = sharp or acid. In contradistinction to nitrogen, it is an extremely active body—that is, it is very ready to form new compounds. We have seen a case of combustion (the combustion of phosphorus) attended with flame, which was brought about by oxygen, as indeed are all the combustions that occur in practical life.

Oxygen also combines slowly with very many substances without producing flame. The rusting of iron, for instance, that is so dreaded by the housewife, depends on the combination of the metal with the oxygen of the air to form iron oxide, or rust as this substance is commonly called.

We shall become acquainted with a whole series of combinations, like the rusting of iron, of bodies of very different kinds with oxygen; such occurrences can scarcely be called combustions, because we associate the appearance of fire with combustion. These processes are called *oxidations*. The terminal syllable in the often used term *oxide* means, as we now readily understand, nothing but a compound with oxygen. *Lead oxide* signifies a compound of lead and oxygen, and *lead superoxide* a similar compound containing twice as much oxygen, and so on.

When an investigation is made of the air that surrounds us, with an observance of all the rules laid down by science,

it is found that air always contains a very little carbonic acid gas and some moisture, besides nitrogen and oxygen; and if a determination is made of the quantity of each of these in 100 parts of air, the following proportions are obtained:

Nitrogen	78·35 parts.
Oxygen...	20·77 „
Water in the gaseous state ...	0·85 part (so-called moisture).
Carbonic acid gas	0·03 „
	100·00 parts.

Chemists call these quantities calculated on 100 parts *percentages*; they say that air contains 78·35 *per cent.* of nitrogen, etc.

It has been found recently that nitrogen separated from air by a chemical method—we learnt to recognise a chemical process a little while ago—is not a homogeneous body, as had been supposed, but that it contains, mixed with it, very small quantities of several other gaseous elements, which have been called *argon*, *helium*, *krypton*, *neon*, and *xenon*. These elements are present in the air in such very small quantities that it is not necessary for us to say more about them.

We are all aware that the ability of the air to take up moisture, and to deposit it again in the form of rain, is of great importance in the economy of nature. In daily life also we make constant use of this capability of the atmosphere to take up water; for on this depends the drying of the wash, or of a floor that has been scrubbed, etc.

We must not forget the modification of oxygen which is called *ozone*, as this substance is often mentioned in ordinary life.

When we have become acquainted with the conception of the atom (see p. 24), we shall be in a position to understand the relations between ozone and ordinary oxygen (see p. 27).

In 1896, Linde succeeded in liquefying air by the use of an extraordinarily ingenious mechanical arrangement. The liquid consists for the most part of oxygen and nitrogen, which can be separated by distillation (see p. 25).

Now that we have got to know the composition of air, the question presents itself why we must have air to live in, for experience tells us that want of air leads to suffocation and cessation of life.

This is explained as follows. The air which we involuntarily breathe in finds its way into the lungs, and there comes into contact with the blood by passing through the walls of the fine capillary veins wherein the blood is circulating. Such thin membranes as the coatings of the veins are quite impermeable by liquids, but allow gases to pass through them freely, or, to use the technical expression, to diffuse through them. When, then, the blood comes into contact with the oxygen of the air by diffusion, the blood absorbs oxygen, and at the same time gives up carbonic acid gas. We should therefore find the expired breath to be rich in carbonic acid; and it is easy to prove experimentally that this is the case.

For this purpose we will draw some external air through clear, filtered lime-water by sucking with the mouth at A (fig. 5). There is so small a proportion of carbonic acid in the air that no visible change is made in the lime-water in the short time during which the experiment lasts; but when I blow expired breath through the same lime-water by means of the small tube *B* (fig. 6), a turbidity, which is visible at

some distance, quickly appears in the liquid. This means that the carbonic acid gas in the expired breath has combined with the lime to form chalk, which, being insoluble in water, is diffused through the liquid as a fine powder.

The following analysis of a sample of expired breath, which had been deprived of moisture, shows how considerable is the quantity of carbonic acid in the breath sent out from the lungs:

Nitrogen	79·58 per cent.
Oxygen	16·04 „
Carbonic acid gas	4·38 „

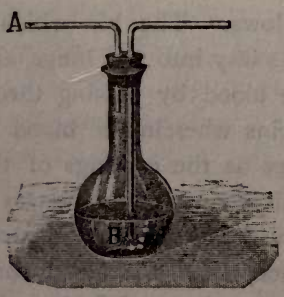


Fig. 5.

Fig. 6.

While the oxygen has been reduced by about one-fifth, the quantity of carbonic acid has been increased about a hundred-and-forty-fold.

The oxygen which has been absorbed by the blood is carried by the blood through the whole of the body, and brings about oxidations. Particularly, it burns to carbonic acid the carbon of many substances—which are naturally always being re-formed by the help of the nourishment taken into the body—and the blood returning to the lungs carries with it this carbonic acid gas, which originates from the

tissues, etc., in the most different parts of the body, and there gives it up in exchange for oxygen.

The continuous oxidation which takes place in the body as a consequence of breathing is accompanied, like every other process of burning—for oxidation is merely another name for burning—with the production of heat; and it is this heat which maintains our bodies at their normal temperature of 37° C. [98·4° F.].

When we consider that the circulation of blood from and back to the heart occupies only about ten seconds in a man, we easily understand how our bodily temperature is kept constant in all parts of the body by this process, notwithstanding that we are continually parting with a considerable quantity of heat to our colder surroundings. In a subsequent lecture we shall discover what weight of carbon must be burnt daily for this purpose. But even now it is clear from what has been said that the supply of carbon compounds in the body must soon be exhausted unless there be sufficient compensation; and hence, as well as to make up for other withdrawals, we are compelled to absorb sufficient quantities of nourishment.

Before leaving our present subject, we shall glance for a moment at the process of combustion, and in the next lecture we shall deal in more detail with the phenomena of flame which accompany combustions, as both of these are conditioned by oxygen, about which we have learnt something.

All the materials used in ordinary life for burning are rich in carbon; wood and turf, for instance, have been used for ages, and in more recent times coal and peat have come into use, as fuel. The process of burning such fuels consists, in the main, in the combination of the carbon of the fuel with

the oxygen of the air to form carbonic acid, while at the same time the small quantities of hydrogen in the materials are burnt to water.

Carbon and oxygen do not combine when cold ; but if the combination is started, the material continues to burn, since the heat produced by the part which is burning suffices to make the neighbouring parts hot enough to begin burning —that is, so hot that combination of carbon with oxygen occurs.

We cannot at present go into the methods that have been so fully developed nowadays for the most economic employment of fuel ; but when we come to speak of the metallurgy of iron, we shall have occasion to learn something more fully of these methods in connection with the processes for manufacturing that metal.

The question as to how combustible material is set on fire, how the burning is generally started, has still to be answered. Nowadays it is very easy : we use matches ; but matches came into use only about eighty years ago. The question must always remain unanswered as to whether primitive man became acquainted with fire by rubbing pieces of dry wood together, or by obtaining it from a tree which had been ignited by a lightning-flash. It is certain that fire can be obtained by rubbing together pieces of wood ; and travellers have found this method in use among distant tribes at the present time. The method, however, requires the wood to be drier than we ever find it in its natural state in our climate. The difficulty of getting fire anew, and therefore the immense importance of maintaining the fire which had been started, explain the fact that all the older races looked on the hearth, where this supreme possession was maintained continuously, as a sacred place.

The process of obtaining fire by allowing the sparks produced by striking a piece of steel and a flint together to fall on to tinder or dry fungus was generally used in the later Middle Ages.

Since the beginning of last century isolated attempts were made to devise a method for getting fire, which could always be conveniently applied, by employing some one of the processes—and there are many of them—in use in chemical laboratories. The results of these attempts were but small, the methods themselves were very inconvenient and untrustworthy, and the apparatus was sometimes absolutely dangerous, until in the thirties use was made of *phosphorus*.

About that time an Hungarian chemist, Johann Jrinyi, hit on the notion of using phosphorus, experiments with which substance he had seen made in a lecture. Sulphur-matches, which were little slips of wood tipped with sulphur, were in common use at that time for obtaining fire; Jrinyi added a little phosphorus to the sulphur, and the lucifer-match was made.

Phosphorus, as is generally known, takes fire when rubbed; the burning is passed on by the phosphorus to the sulphur, and from the sulphur to the wood. It was of course not so easy to surmount the technical difficulties and to manufacture really good lucifer matches. But after a time matches of unexceptionable quality were prepared.

As a fire-producing material the lucifer-match left nothing to be desired; but these matches had other properties which have led to their replacement of late years by what are generally called safety-matches.

Phosphorus is extremely poisonous; the lucifer-match placed the general public in possession of this dangerous

substance; and the substance had also deadly effects on the workers in match factories, many of whom suffered from terrible diseases in their bones.

Ordinary phosphorus is yellow; but it possesses the remarkable property of changing into a red powder, known as *red phosphorus*, when it is heated for some time to about 250° C. [482° F.] in a closed space—heated in the air of course it burns—such as a vessel with a tightly fitting cover. This transformation can be shown here easily in the following way. A small quantity of yellow phosphorus is placed in the glass tube A (fig. 7), and the tube is closed by fusing together the glass at the open end; the tube is then suspended in a wider tube, wherein is placed a liquid that boils at 250° C. [482° F.]. The liquid is now caused to boil, and the tube A is thus surrounded by the vapour of the boiling liquid, which soon heats A to 250°, and we see the yellow phosphorus gradually changing to a red mass.

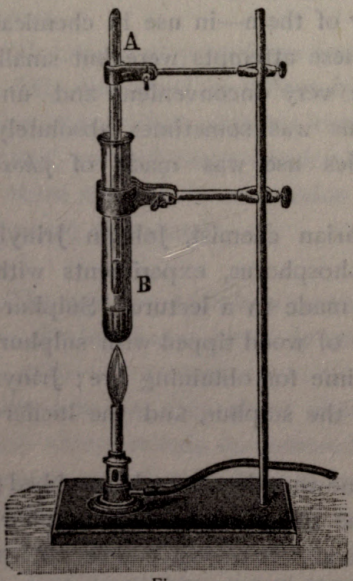


Fig. 7.

Now red phosphorus is not poisonous, and it is also much more difficult to ignite than yellow phosphorus; it is, indeed, so uninflammable that it does not take fire when rubbed on any casual surface. To ignite red phosphorus by friction requires rubbing on a surface containing substances rich in oxygen. The mixture used for making the heads of safety-

matches which are ignited by rubbing on a surface prepared with red phosphorus consists of 32 parts chlorate of potash, 12 parts chromate of potash, 32 parts peroxide of lead, and 34 parts sulphide of lead ; the first three of these substances are characterised by the large quantities of oxygen they contain.

LECTURE II

Nature of flame : (1) Candles—Composition of fats—Oils—Petroleum—Hydrocarbons—The elements—Tetravalency of the atom of carbon—Chemical formulæ—The atom and the molecule—Distillation—Petroleum ether—Vaseline—Paraffin—Ozone—Manufacture of coal-gas—Nature of flame : (2) Cooking by gas—Incandescent gaslights—Electric furnace—Acetylene.

IT is well known that the burning of substances which contain carbon serves not only for the production of heat, but also for lighting purposes. But flame is produced only by those carbon-containing materials which are converted into gas or vapour when they are burnt ; this will be proved by experiment very shortly.

Compounds which contain very much carbon, such as wood, coal, or tallow, are not, indeed, themselves volatile, but they burn with a flame because they give off combustible gases when they are heated. The flame is therefore nothing else than a burning gas which is constantly being produced from the material.

If we now set fire to a piece of wood, we see that it burns with a flame ; but if we have previously removed from the wood everything that will volatilise, by heating the wood very strongly out of contact with the air, we find that the wood charcoal thus produced will not burn with a flame.

It is possible to draw the gas out of a flame—out of a

candle-flame, for instance—and then to burn the gas. The method of doing this is as follows. We introduce a glass tube into the flame ; one end of this tube is drawn to a point, and the other passes through a cork which is fitted into a cylinder quite filled with water. Another glass tube passes through the cork, and reaches to the bottom of the cylinder ; this tube is connected with a piece of caoutchouc tubing, and the glass and caoutchouc tubes are filled with water, and so

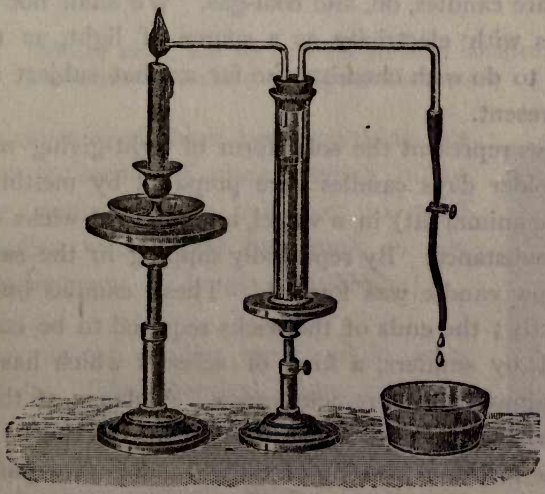


Fig. 8.

act as a syphon (see fig. 8). Water is now allowed to flow slowly from the caoutchouc tube by partially opening a pinch-cock placed on this tube; suction is thus produced at the point of the glass tube in the candle-flame, and some portion of the gases and vapours is thus drawn from the flame into the cylinder. As the process continues the flame becomes conspicuously smaller, because we are removing part of the material which feeds it. It is necessary to suck gently to avoid getting air into the cylinder along with the vapours from the flame. When the cylinder is filled with the gases

from the flame, the cork is removed, and a light is brought to the mouth of the cylinder ; the contents of the cylinder—that is to say, the gas derived from the candle—take fire and burn quietly. This experiment furnishes a proof of the justness of the statement made at the beginning of this lecture.

Let us now get some fuller knowledge respecting the three chief materials used for lighting purposes. These three substances are candles, oil, and coal-gas. We shall not concern ourselves with electricity as a source of light, as this has nothing to do with chemistry so far as that subject interests us at present.

Candles represent the solid form of light-giving materials. In the older days candles were prepared by melting tallow (or crude animal fat) in a vessel, and dipping wicks into the melted substance. By repeatedly dipping in the same wick the tallow candle was formed. These candles burnt very imperfectly ; the ends of the wicks required to be constantly removed by snuffers, a kind of scissors which has already passed almost out of remembrance. A glance at the tallow candle which was lighted at the beginning of the lecture will show the mode of burning of these candles (compare fig. 9). The reason of the imperfect burning of these candles was as follows. We know that the tallow is volatilised by the high temperature of the flame ; this volatilisation of course takes place from the wick, which sucks up the fat that is melted in contact with it where the flame produces heat sufficient to cause the volatilisation ; the gases thus produced make their way into the air, and are burnt there by the aerial oxygen, which converts the carbon into carbonic acid and the hydrogen into water. The wick itself does not come into contact with the air, as the ascending gases cut it off therefrom ; the wick is therefore carbonised by the heat, because the carbon of the

wick cannot burn for lack of oxygen, and after a time the carbonised end of the wick prevents the flame from burning symmetrically. Symmetrical burning begins again when the end of the wick is removed, or, as used to be said, when the candle is snuffed.

All this seems to us to-day rather unimportant, as we no longer suffer personally from the inconvenience of constantly snuffing our lights. Goethe, however, could still say in his maxims in rhyme:

> Wüsste nicht, was sie besseres erfinden konnten,
> Als wenn die Lichter ohne Putzen brennten.

And it must surely have been anything but pleasant to break off one's reading of an evening, perhaps every half-hour, to snuff the candles, whose light had sunk so low that reading was no longer possible.

Fig. 9.

These tallow candles were made from natural fat. The chemical examination of fat, which began to have successful results about the end of the eighteenth century, led at last to the stearin candles we use to-day. This investigation showed that all fats which are derived from animals or plants can be resolved into two main constituents —namely, into several fatty acids and *glycerin*.

In the fat of animals, in oxen-fat for example, three fatty acids—called *stearic*, *palmitic*, and *oleic acids*—are found in combination with glycerin. The two first-named acids are solids, the third is a liquid; and the more *oleate of glycerin* a fat contains the less solid it is. Swine-suet and goose-suet, for instance, are very rich in the last-named substance. Fat is easily split up into its two constituents by technically

applicable processes, and the mixture of the three fatty acids thus obtained is freed from oleic acid as far as possible by pressure. The white cake which remains is further purified, and from this stearin candles are made. Before melting and running into the form of candles, 10 per cent. of *paraffin*—we shall learn immediately what that is—is added to the cake, and this produces the homogeneous white wax we commonly see in stearin candles. A mixture of stearic and palmitic acids without this addition crystallises easily as it cools, and candles made from such a mixture show a certain streakiness, which is prevented by the addition of paraffin.

The wick, round which the mixture is poured in making the candles, is tightly twisted on its axis, and this twist remains when the material hardens; the result is that when the candle is gradually consumed, after it has been lighted, the wick is always bent, and by this means the end of the wick is constantly and automatically kept out of the flame. Now there is sufficient oxygen outside of the flame to insure the complete combustion of the wick, and in this way an unburnt head never gets formed, snuffing is not needed, and stearin candles burn perfectly symmetrically. This artifice could not be applied to tallow candles, because the material of which they were made was too soft to maintain the necessary twist in the wick.

We must also make mention of wax candles. Bees'-wax, which is an animal fat, is very like other fats in its chemical relations. This wax consists of fatty acids and an alcohol; glycerin is also, chemically, an alcohol. The fatty acids in bees'-wax are *cerotic* and *palmitic acids*: they are combined in the wax with *myricyl alcohol*. As bees'-wax is harder than tallow, candles made from that wax are found to be better than those made from tallow.

Olive oil and oil of rape-seed were the liquids most commonly used as burning materials forty years ago; wicks were dipped into the oils, and they were burnt in lamps adapted for the purpose. These oils are closely related chemically to the fats; they consist of fatty acids and glycerin. The fatty acids present in them in greatest quantity are of course liquids.

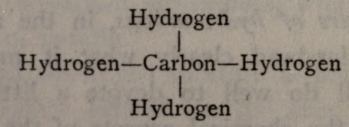
Petroleum, which is now much more used than the oils we have been speaking of, is quite a different substance; it is a mixture of *hydrocarbons*. As we often find this expression, *mixture of hydrocarbons*, in the newspapers, we must try to understand clearly what it means; for this purpose we shall do well to devote a little time to the consideration of the chemical aspects of the matter.

In chemistry one speaks of the elements. By that term is understood those constituents of bodies which have not been separated into simpler substances in any of the many attempts that have been made to effect such separations. About eighty such elements are known. Most of them are very rare; only about twenty play a part in daily life; and the whole world with which we have ordinarily to do is constructed from these few building stones. Hence we should expect to find, as indeed we do find, that the variety of their combinations is astonishingly great.

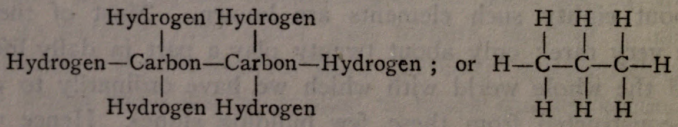
Now carbon is the element which far surpasses all the others in its power of forming combinations; the variety of ways wherein atoms of carbon are able to combine with the atoms of other elements, or with other atoms of carbon, is greater than the ways of combination of all the other elements taken together. And when nature created living things she made use of carbon. Therefore it follows that carbon is present in every substance which is connected with

the existence of life; be it the seed of an apple, or the flesh or the bony skeleton of an animal, all are interpenetrated with compounds of carbon.

The quite innumerable number of carbon compounds may be brought into an easily comprehended system by making the compounds with hydrogen the starting-point of the complete scheme. One atom of carbon is able to bind to itself four atoms of hydrogen; or, as is commonly said, the atom of carbon is tetravalent. This may be represented as follows:



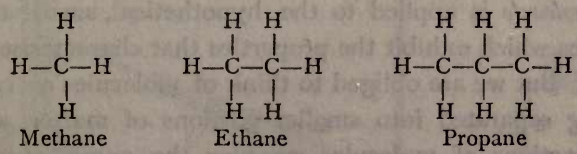
Now we have already mentioned that carbon atoms are able to form connected chains with one another; and this leads to the formation of new hydrocarbons, in which the carbon atoms are held together, besides being in combination with atoms of hydrogen. Thus:



In these instances we have connected together as many as three atoms of carbon; and we may go further—these chains have been formed with sixty atoms of carbon. Such rows of atoms may ramify in the most different directions; the carbon chains may, indeed, return upon themselves in the form of rings—with which we shall have to deal in the last lecture, where some of the more recently introduced therapeutic agents will be considered. It is very evident, then, that the number of possible hydrocarbons is immense.

In representing the three hydrocarbons referred to above

we began by writing the names of the elements in full, and then we shortened these names by using only the initial letters of them without interfering with the intelligibility of the *chemical formulæ* of the compounds; for the way of writing the third hydrocarbon is indeed an actual chemical formula. The letter *C* stands for carbon, and *H* for hydrogen; and these letters are used as the symbols for those elements in all languages. Employing these symbols, and adopting the same method of representation as before, we have the following formulæ for the three hydrocarbons, which are the formulæ in common use in the chemical text-books:



American petroleum contains many hydrocarbons with "*single chains of carbon atoms*," belonging to that series the initial members of which we have here formulated, and the technical names of which we have given.

The first member of this series is a gas; it contains much hydrogen, which is the lightest element known. This hydrocarbon is formed in the decay of vegetable matter in presence of much water; it is found, therefore, in the gases arising from marshy places, and for this reason it is called *marsh-gas*.* Chemists give to it also the name *methane*.

The collection of this gas from a marsh is an easier matter

* It appears, from a letter of the celebrated French naturalist Volta to a French scientific friend, that Volta knew in 1776 that every marsh gave off this gas, or, as we might say to-day, was a kind of gas factory. The term *volt*, applied to-day to the pressure of an electric current, is derived from the name of the Italian naturalist; as the term *ampère* used in measuring the quantity of the current, recalls the French physicist of

than one might be ready to suppose. It is only necessary to sink a large funnel in the marsh, with the wider open end downwards; the gas then collects in the funnel, and bubbles upwards, and it may be collected in a suitable apparatus connected with the narrow end of the funnel.

The second hydrocarbon, *ethane*, whose molecule contains six atoms of hydrogen, is a gas; as is also the third, *propane*, which contains eight atoms of hydrogen. This third hydrocarbon is found dissolved in crude petroleum.

Before proceeding further we must give some explanation of the term *molecule*, which has just been employed. The word *molecule* is applied to the, hypothetical, smallest parts of bodies which exhibit the properties that characterise these bodies. But we are obliged to think of molecules as capable of being separated into smaller portions of matter, and to these fractions of molecules we give the name *atoms*. A molecule is composed of atoms which may be all of one kind, or of different kinds; in the former case we have the molecule of an element, in the latter we have the molecule of a compound.

When we come to that hydrocarbon which contains four atoms of carbon, we find that it is a liquid; a liquid, it is true, which boils at 1° C. [33·8° F.]. In keeping with this, it is found that the greater the number of carbon atoms in the molecule of a hydrocarbon the higher is the boiling-point of the compound; for instance, *hexane*, a hydrocarbon with six carbon atoms, found in petroleum, boils at 70° C. [158° F.].

that name. These terms are constantly heard since the introduction of electric lighting. Accurate analyses of marsh-gas, on which we base the statement that it consists of four atoms of hydrogen combined with a single atom of carbon, were carried out about forty years after the discovery of the gas.

As the quantity of carbon increases the compounds become less fluid, and at last even solid.

Large quantities of hydrocarbons are present in crude petroleum. When this is distilled, that is, is heated so that whatever is volatilised at the higher temperature is again cooled by means of a condensing arrangement and is then again liquefied—somewhat in the manner shown in fig. 10—

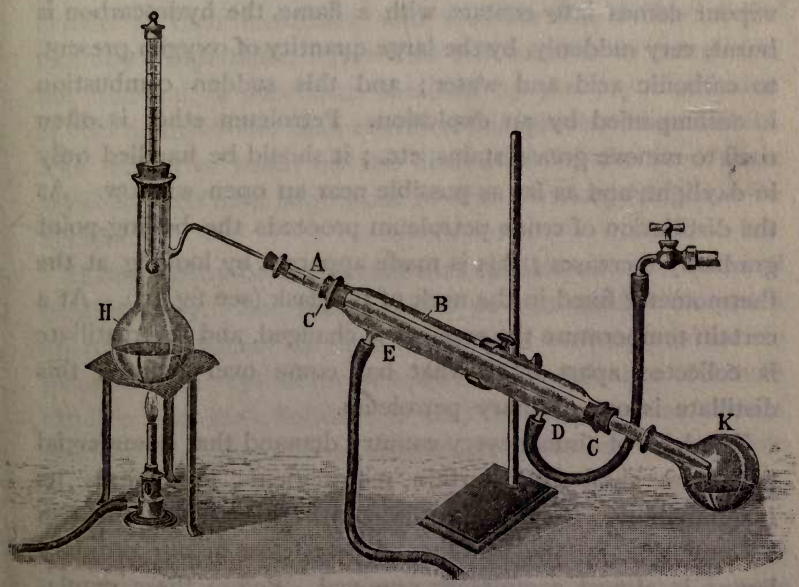


Fig. 10.

The distillation apparatus presented here is that commonly used in laboratories. The liquid is heated to boiling in a flask, H, and the vapour which rises from the boiling liquid passes through the side-tube, sealed on to the neck of the flask, into the condensing tube, A, which passes, through the corks, C, into a wider tube, B, through which a stream of cold water is kept constantly passing by means of the rubber tubing, D and E. The vapour is thus cooled, and in consequence of this it becomes liquid again, and finds its way in drops into the receiver, K. A thermometer fastened into the neck of the distilling-flask serves to determine the temperature whereat the distillation is proceeding. The apparatus used in manufactories is made of metal, and is of course larger, but the principle is the same.

the gaseous compounds are first given off; then come the lower boiling portions which are known commercially as petroleum ether.

Petroleum ether often gives rise to explosions; the reason of this is as follows. The volatility of this substance is so great that it very easily evaporates into the air—say, into the air of a room; if now this mixture of air and hydrocarbon vapour comes into contact with a flame, the hydrocarbon is burnt, very suddenly, by the large quantity of oxygen present, to carbonic acid and water; and this sudden combustion is accompanied by an explosion. Petroleum ether is often used to remove grease stains, etc.; it should be handled only in daylight, and as far as possible near an open window. As the distillation of crude petroleum proceeds the boiling-point gradually increases; this is made apparent by looking at the thermometer fixed in the neck of the flask (see fig. 10). At a certain temperature the receiver is changed, and the distillate is collected apart from what has come over before; this distillate is our ordinary petroleum.

The laws of almost every country demand that commercial petroleum shall fulfil certain requirements as regards its inflammability, and these requirements are such that the risk of explosion by the burning of petroleum in our ordinary lamps is almost completely removed. Before these regulations were put into practice it often happened that petroleum contained some of what we now call petroleum ether, and that this volatilised in the reservoirs of the lamps. As soon as the mixture of this vapour and the air in the reservoir became of the proper composition, it ignited at the flame of the lamp, an explosion took place, and the lamp was shattered.

Those portions of crude American petroleum which remain when the petroleum oil is distilled off have the consistence of

butter; they are worked up into vaseline. The residues after the distillation of petroleum oil from Caucasian petroleum [and from the oil obtained by distilling shale] are used as lubricating oils for machinery.

The substance already referred to under the name of paraffin is a mixture of hydrocarbons which contain much carbon in their molecules, and are therefore solids at the ordinary temperature. These do not come from petroleum, but from tar, a substance obtained by the dry distillation of coal or shale—we shall consider this process immediately. The industries based on the distillation of coal and shale are conducted on a large scale in Mid-Germany [and also in Scotland].

It can readily be understood that candles may be made of paraffin only. But such candles do not meet with much approval, inasmuch as their transparent whiteness is not so pleasant to the eye as the opaque white appearance of stearin candles, and also because, if they are as long as stearin candles, they generally become bent, as they burn, from their own weight.

Now that the conceptions of the atom and the molecule have been explained it is not difficult to understand more fully than before (see p. 9) the nature of ozone.

Ozone occurs in the atmosphere along with ordinary oxygen. Each minutest portion of oxygen in the atmosphere, each molecule of oxygen, consists of at least two atoms. We must ascribe to all elements a capacity to combine with other elements; otherwise each element would remain for ever apart from all the others, and no compound of any kind could be produced. Now if elements (oxygen, for instance) are found free in the atmosphere, the striving of their atoms to enter

into combination is satisfied by the mutual union of atoms of the same kind. Thus are produced the molecules of ordinary oxygen, each composed of two atoms. And it happens that, under the influence of electric sparks, and on a large scale during thunderstorms (and there are also other causes of the occurrence), three atoms of oxygen link themselves together. This combination of three atoms is not, however, very stable, and the third atom is ready, when opportunity offers, to be disengaged and to combine with atoms of other elements. This modification of oxygen, the smallest particle of which is composed of three atoms, is called ozone.

In speaking of materials used for giving light, we now come to the consideration of coal-gas.

When such a substance as wood, peat, or coal is placed in a closed iron tube like that represented by A in the figure (fig. 11), and the tube is heated very highly,* whatever in the material is volatile at the temperature employed will be driven out and will pass through the exit tube into the vessel C. In this process the substance heated is said to be submitted to dry distillation. Those portions of the substances volatilised from the wood or coal which are liquids at the ordinary temperature will collect, in the form of tar and what is called ammonia water, in C, while that which is gaseous at the ordinary temperature will pass through D, and will be collected in the glass jar E, which here serves as a gasometer. The glass jar E may well be called a gasometer, inasmuch as our apparatus represents, on a small scale, the main parts of a gas manufactory. In an actual gas-works only gas-coal is used as the material; and in place of large iron tubes, retorts of fire-clay are employed, because these better withstand the continued action of the heating furnaces.

* For this purpose we use a long gas furnace.

One hundred kilograms of good gas-coal yield from 28,000 to 30,000 litres of gas weighing about 18 kilograms, and about 5 litres of tar and ammonia water, while about 70 to 75 kilos. of coke remain in the retorts. [One ton of good gas-coal yields about 10,000 to 11,000 cubic feet of illuminating gas, about 10 to 13 gallons of gas-liquor, and from 1,000 to 1,500 lbs. of coke.]

On the large scale the tar is got rid of by cooling—the flask C fulfils this purpose in our small-scale experiment; after this the gas is brought into contact with water—it

Fig. 11.

is washed, as the expression goes. Those constituents of the gas which are soluble in water are thus removed. The most important of these, so far as quantity goes, is ammonia; were this allowed to remain in the gas the quality of the gas would be deteriorated.

Ammonia gas is composed of nitrogen and hydrogen; these elements are present in gas-coal in the form of very complex compounds, which are decomposed at the high temperature to which the retorts are subjected, with production of the simpler compound ammonia. Ammonia gas is very soluble

in water; in this dissolved form it is known to every one as the very sharply smelling "*spirits of hartshorn.*" We shall see later what uses are made of the large quantities of ammonia that are obtained from the gas factories of the world.

In the apparatus which we used (represented in fig. 11) a flask, D, was placed between C and the gasometer. This flask represents the vessels employed on the large scale for purifying the gas; these are filled with the purifying material, which is for the most part a mixture of slaked lime and oxide of iron. The slaked lime serves to remove carbonic acid from the gas by combining with it to form chalk; the presence of carbonic acid cannot be prevented entirely in the process of manufacture. We learnt in the first lecture to use the formation of chalk as a means for detecting carbonic acid in expired breath. Inasmuch as carbonic acid is the final product of the burning of carbon, this compound cannot itself be burnt; if, therefore, it is left in coal-gas, the gas is thereby diluted and deteriorated. The oxide of iron in the purifiers is for the purpose of withdrawing gaseous compounds of sulphur from the coal-gas; it does this by combining with the sulphur of these compounds to form sulphide of iron. If any sulphur is left in gas, this sulphur burns, when the gas is lighted, to sulphurous acid, which is a gaseous body with a pungent smell well known to every one as the smell of burning sulphur; some of the sulphur is also burnt to sulphuric acid at the high temperature of the flame of coal-gas.

These purifiers remove almost all the sulphur from the gas, except that which exists in the form of a compound called bisulphide of carbon. The quantity of this compound in coal-gas is extremely small; but its complete removal on the large scale remains to-day an unsolved problem of the gas trade.

When the gas has been purified in the way described it is

collected in gasometers, and it is conducted from these in pipes to the places where it is to be used.

The following analysis will give an idea of the composition of coal-gas:

Hydrogen	45·2	per cent.	by volume.
Methane (see p. 23)	35·0	„	„
Other hydrocarbons	4·4	„	„
Carbon monoxide	8·6	„	„
Carbonic acid	2·0	„	„
Nitrogen	4·8	„	„
	100·0		

When coal-gas is burnt, carbonic acid is produced from the carbon, and water from the hydrogen, of the gas; on account of the high temperature the water is produced in the gaseous form. Thus coal-gas is almost wholly changed, by burning, into two odourless, colourless gases. Besides these gases, the air of rooms wherein coal-gas is burnt contains a little sulphurous acid gas, produced by the burning of the traces of sulphur-containing compounds in the gas. It is on account of this sulphurous acid gas that window plants do not flourish well in rooms wherein coal-gas is burnt. The small quantities of sulphurous acid produced by burning coal-gas are found, fortunately, to be quite harmless to human beings.

It has been said above that part of the sulphur in gas is burnt to sulphuric acid. This result of the combustion is made apparent in the spots that appear on the globes of gas-lamps when these globes are not very frequently cleaned. Small drops of liquid sulphuric acid settle on the globes, and, as sulphuric acid is an extremely corrosive, that is destructive, substance, the particles of dust that fall upon the globes are charred by it. Hence it is that the globes of such lamps get gradually covered with brownish specks; such specks are

not seen on the chimneys used on lamps for burning oil or petroleum, inasmuch as these substances do not contain sulphur.

What remains to be said about the nature of luminous flame can now be made clear and illustrated very conveniently in connection with the flame of coal-gas.

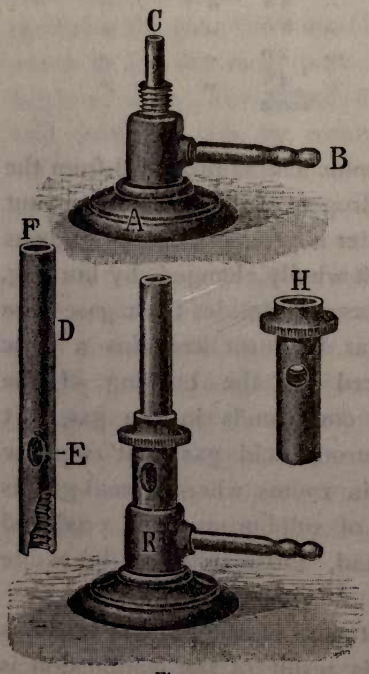


Fig. 12.

The presence of carbon in the luminous flame is demonstrated by holding a porcelain plate in the flame, when, on account of the cooling effect of the cold surface, carbon is deposited on the plate in the form of soot. This carbon was separated in the flame itself by the heat of the flame; and as at the same time it was raised to a white heat it caused the luminosity of the flame. When this carbon reaches the edge of the flame and there comes into contact with the oxygen of the air, it is burnt to carbonic acid, and in this form it escapes into the surrounding atmosphere. It can easily be shown that this is actually what occurs. Those of you who cook by gas—a method which is rightly coming more and more into use in the kitchen—always use non-luminous gas-flames, which do not cover the cooking-vessels with soot because no separation of carbon occurs in such

flames. Chemists have employed gas, when it was to be obtained, for heating purposes for the last fifty years; they make use of the burner invented by Bunsen, which burner has of late years been adapted to apparatus for cooking by gas (see R, fig. 12). In a Bunsen burner the gas issues from a narrow opening (C, fig. 12). If it is lighted at this opening the gas burns with the ordinary luminous flame; but if there is placed over this opening a tube with holes for admitting air near to the opening from which the gas issues (see D, E, F, fig. 12), the gas streaming through this tube is able to carry a little air with it. If we now light the gas at the open end of the tube the flame is non-luminous, because there is so much air mixed with the gas that the oxygen in this air suffices to cause combustion of all the carbon in the gas; at the same time, a great heating effect is produced. If the holes in the tubes are closed by turning the short outer tube (H, fig. 12), the flame burns luminously, as we should expect.

Fig. 13.

The arrangement in all gas-cooking apparatus is exactly similar to that used in the Bunsen burner. You see that the gas issues from a small opening immediately in front of the stop-cock, and near this you see several openings for the entrance of air into the wider tube which conducts the mixture of gas and a little air to the place where it is to be burnt. Should too much air get into the tube by accident we should have, of course, an explosive mixture; were this ignited the gas would burn for a moment, and the flame would then strike back to the opening by which the coal-gas enters the tube, where it would burn, as at this point it would come into contact with the

external air, which would still be needed to maintain the combustion.

As has been already indicated, a non-luminous gas-flame gives out very much heat, because of the rapid combustion that is proceeding in it. If we hold a bundle of platinum wires in such a flame, the platinum, which is not itself in the least changed at this temperature, becomes heated to full redness and radiates light. The latest important advance made in lighting by gas—namely, the incandescent gas-light—exhibits this process in a very complete way. In the incandescent gas-light (see fig. 13), the flame is rendered non-luminous by the admission of air, in the same way as in the Bunsen burner. We always notice several small openings—generally four—in these incandescent lamps, placed near the point where the gas enters the burner. The very hot, non-luminous flame heats a hollow mantle suspended in it to a very high temperature. This mantle is saturated with certain oxides, partly the oxides of rare elements such as oxides of cerium and thorium, which have long been known to emit very clear light when they are heated.

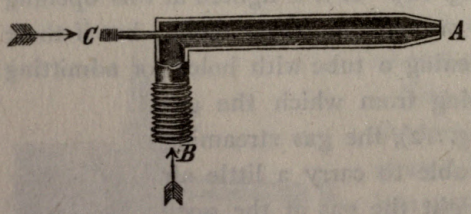


Fig. 14.

Auer was the first to turn this property successfully to account in daily life. He busied himself with the matter for a long time. So long ago as 1885 he had constructed an incandescent lamp for lighting rooms; but the lamp was made serviceable only in October 1891, and since that time it has been much improved by him, especially by so mixing the most appropriate oxides in the mantle as to produce a white light pleasant to the eyes, in place of the somewhat faded,

moonshiny colour which the light possessed when it was first introduced.

Daily experience shows us that high temperatures have different effects on different substances. Since we have been able to command very high temperatures, it has become possible to prepare many compounds which could formerly be obtained with great difficulty, or not at all. Temperatures higher than any formerly known are reached between the carbon points of the electric arc-lamp. When, for example, a mixture of charcoal and chalk is brought into the electric arc —the apparatus is called an electric furnace (see fig. 15)—a

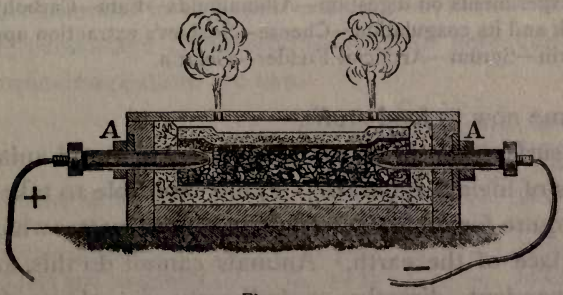


Fig. 15.

reaction happens between the two substances, and a new substance called calcium carbide is produced. This substance —it was first prepared in quantity by Moissan—is very stable towards heat, but it readily reacts with cold water and produces a gas, which has been known for a long time, and is called acetylene. This gas, which used to be costly, is now produced at so cheap a rate that it is used for lighting purposes.

By burning acetylene in oxygen, in a specially constructed burner, shown in fig. 14 (acetylene enters at C, and oxygen at B, and the mixture is burnt at A), an exceedingly hot flame is obtained; this flame is used for firmly joining sheets of iron without solder. The flame is run along the edges of the plates, the iron melts, and a compact homogeneous plate is produced.

LECTURE III

Food of Plants—Manuring—Fallow land—Artificial manures—Bones—Superphosphates—Potash salts—Manuring with nitrogen—Bases, acids, and salts—Mother-liquor—Food of men and animals—Experiments on digestion—Albuminoids—Fats—Carbohydrates—Milk and its coagulation—Cheese—Soxhlet's extraction apparatus—Fibrin—Serum—Artificial Fodder—Gelatin.

WE come now to food-stuffs.

The surface of the earth whereon plants and animals live consists of lifeless materials. Plants are able to take all that they require for their life from this lifeless matter which forms the surface of the earth. Animals cannot do this, and they are dependent, directly or indirectly, on plants for their nourishment. A tree, for instance, stands in the same place for hundreds of years, and nature supplies it with all that is needed for its existence; rain brings the moisture the tree requires, and the carbon which it needs for forming wood and all that complex structure which renders its life possible it takes chiefly from the carbonic acid of the air. The leaves of plants, and, in all probability, more especially the green parts of the leaves, which are called chlorophyll-grains, have the power of decomposing carbonic acid, which itself consists of carbon and oxygen, in such a way that the leaves make use of the carbon and give out the oxygen. This is the more remarkable as carbonic acid is a very stable gas, which can be separated into its constituents in the laboratory only with

difficulty, and is itself produced, as we know, at the high temperature of burning flames.

The soil whereon the plant grows furnishes the other inorganic compounds—that is to say, the compounds derived from lifeless matter—that are required by the plant. We are enabled to see these compounds by burning the plant—wood, for instance—when they remain as ashes.

If we examine such plant-ashes more narrowly, analyses of them give us the following results. The quantity of ash of a rye-plant, for instance, when the plant is in bloom, amounts to 6·38 per cent. of the weight of the plant; the ash of ripe rye-grains amounts to 1·93 per cent. The ash itself has the following percentage composition—we shall here employ the most simple designations we can.

	Composition of the Ash of Rye-plants. Per cent.	Composition of the Ash of Rye-grains. Per cent.
Potash salts	37·16	34·50
Common salt	0·76	0·90
Oxide of iron	0·50	0·20
Lime and magnesia	12·32	14·13
Phosphoric acid	20·35	47·52
Sulphuric acid	4·03	—
Silica	24·88	2·75
	100·00	100·00

All these things must be contained in the soil if such a plant as rye is to thrive thereon. There is never any lack of some of these constituents, such as silica, which is the chemical name for pure sand, and oxide of iron. On the other hand, investigations, the consequences of which were fully elucidated for the first time by Liebig, have taught us to recognise that unless the soil is to become exhausted we must add to it *phosphoric acid*, *potash salts*, and *nitrogen*.

We have not as yet become acquainted with the last of these substances in this connection, but we shall get to know

something about it. When we consider that all the civilised peoples of whom we know anything have practised agriculture from the earliest times, and further, when we think that Liebig was the first, in the forties of last century, to make clear what part the soil has to play, we must certainly be astonished that such an immense time was needed for mankind to come to this knowledge, and we must the more admire Liebig when we consider that at no time of his life was he a farmer. Even Thaer, who was the great reformer of agriculture, and was the first to endeavour in a serious way to place this industry on a scientific foundation, and who indeed obtained very remarkable results about the beginning of last century—even Thaer regarded the ash-contents of the plant as only casual constituents. According to him plants flourish the better the deeper is the layer of humus in the soil; he arrived at quite a false conception of the state of affairs regarding the nourishment of plants. It may be said without exaggeration that until Liebig discovered the essential facts all agriculture had been merely a robbing of the soil, whereby in the course of time many parts of the earth had been utterly exhausted.

The observation was made at a very early period that if the same crop is taken from the same plot of ground for several years in succession the yield gradually diminishes; and for this reason the cultivation of crops has always been alternated in a certain cycle.

Thus we find that the books on agriculture which have come down to us from the ancient classical times recommend a rotation of crops; and the works on agriculture which were written before the time of Frederick the Great contain essentially nothing that is not to be found in these ancient writings. We can scarcely speak of progress in agriculture during these ages.

The reason of the increased productiveness insured by practising a rotation of crops lies in this, that, because the composition of the ashes of the various plants is not the same, so the exhaustion of the soil does not take place in the same direction in every year. On the other hand, fields have been manured since ancient times with the waste products at the disposal of the farmer, so that, without exactly knowing why, what had been taken from the soil was returned to it, and the productiveness of the soil was thereby found to be improved. But, as much of the produce of the farm is sold, a certain quantity of the inorganic salts will be removed annually from the soil without being returned thereto, and for this reason a diminution in the fertility of the soil must take place, notwithstanding the manuring to which the soil is subjected. Ordinary experience proved this to be the case, but no one was able to find the true explanation.

This leads us to the so-called fallow system of farming. When fields had borne crops for some years they were allowed to remain for a year uncultivated, and this had a real effect in increasing their fertility afterwards. Why this should be so cannot be understood without further explanation. For, if one may put it in this way, neither phosphoric acid nor potash salts are rained from the heavens, and none of these salts comes into the soil from the outside by letting that soil lie fallow; no improvement of the soil takes place in this way.

The good results of the system of fallow depend on the following considerations. The greater part of the phosphoric acid and of the potash salts in the soil is present as compounds insoluble in water. Such insoluble substances cannot be made use of by the roots of the plants, as these are only able to absorb substances in solution. Now the moisture in the soil, together with the carbonic acid circulating therein, which is derived from the air, seize on these insoluble compounds

and change them into soluble substances. If, then, the store of material that has thus been made available for the nourishment of plants is not withdrawn from the soil for a year, this store suffices, along with that which is dissolved every year, to make it possible after a time to reap a profitable harvest.

It was discovered about the year 1750 that the fields might be sown with clover in the year in which they had until then been allowed to lie fallow without any noticeable diminution in the yield when corn was afterwards raised. What was for that period a great advance was thus made, as more cattle could now be reared, and so more manure could be obtained for the ground ; and when the soil became unsuited for growing clover, as experience soon showed did occur, it was possible to raise peas, beans, potatoes, and the like. In this way arose a regular rotation of straw and green crops, with a periodical interpolation of clover.

If the system of fallow was not required, this was only because the different crops, as has already been pointed out, use up very different quantities of the particular inorganic food-salts, so that, by a judicious system of rotation, only small quantities of those salts which are much used were removed throughout the year by cropping the soil. But, without being aware of it, agriculture committed a greater robbery of the inorganic salts of the soil than before ; for in order that one field might be more richly manured the neighbouring field was made poorer. The effects of this injury to the soil would have become apparent in our time had not the connection between the soil and the crops been made clear by Liebig, and had not a cheaper substitute for the inorganic salts removed from the soil been obtained from the store that exists in lifeless materials. By this means the system of fallow was made practically superfluous.

The loss which the soil suffers by the removal of the harvest is made good to-day, in so far as this loss is not covered by the natural manure, by the addition of artificial manure. Indeed, as any quantity of artificial manure is at our disposal, the productiveness of the soil can be very much increased by using as much of this manure as experience has shown to be expedient. The merit of Liebig was most conspicuous in this method, which is the only rational one, of giving back to the soil, by artificial means, the compounds and substances which the growth of the plants had withdrawn from it. Hence it is that we have recourse nowadays to the chemical manufactory for the preparation of artificial manures.*

The following are the chief sources whence phosphoric acid can be obtained cheaply—if the cost of the phosphoric acid were great it would be useless to the farmer.

First of all, from bones. These consist for the most part of phosphate of lime ; besides this they contain fat and gelatinous substances. The fat is extracted from bones nowadays with petroleum ether, and is used for making candles and soap.

* Properly prepared mixtures, soluble in water, of the foodstuffs most valuable to plants, especially those required by garden- and pot-plants, are now to be had in the market and have come into ordinary use. In using these mixtures for manuring plants in pots great care must be taken to add the proper quantity, as the effect of too much of such mixtures is very injurious. About half a gram of such a mixture of food-salts should be used for each kilo. of earth in the pot, and this half-gram should be dissolved in half a litre of water. [About 7 grains per 2 lbs. of earth, dissolved in a pint of water.] If more concentrated solutions than this are used the roots of the plants are likely to be corroded, or even killed. The quantity named above should serve for a year ; and half of it should be applied each six months. The quantity of food-salts to be used in a garden depends on the depth to which the soil is trenched. If, for instance, a square metre is dug 20 centimetres deep, then (using the proportion 1 : 2,000) a solution of 100 grams of the soluble food-salts should be employed. [Eleven square feet dug 8 in. deep require a solution of 3½ oz. of the food-salts.]

We have already spoken of candles, and we shall have something to say of soap later. The process for the extraction of gelatin from bones will not be described, as the understanding of it requires a large amount of preliminary explanation.

When bones are calcined in a closed vessel with an exit tube for the escape of vapour, similar to that wherein coal is heated in the manufacture of gas, a black mass is left behind corresponding with the coke left in the gas-retorts; this black residue is known as bone charcoal [or animal charcoal]. This animal charcoal possesses the property of removing the colour from coloured solutions; for instance, if red wine is shaken with animal charcoal and then filtered, a clear, colourless liquid, like water, is obtained. This property of animal charcoal is made use of in many industries; for instance, sugar-syrup is decolourised by this method. Blacking for shoes is made by mixing very finely ground animal charcoal with some suitable kind of grease.

If bones are calcined in the air the whole of their carbon is burnt away, and a white substance remains. Calcined bones form the material from which phosphorus (which we heard about in the lecture on matches) is manufactured; they are also used in the preparation of *milk glass* (see Lecture X.).

Another source of phosphoric acid is the phosphate of lime which is found very widely distributed over the surface of the earth. This substance, which is known as *phosphorite*, contains varying quantities of impurities. Large quantities of phosphorite are found in Florida, in North America, containing on the average about 82 per cent. of phosphate of lime; and as the impurities in the Florida phosphorite do not materially affect its chemical treatment, this American phosphorite finds a market everywhere.

Guano was once of much importance; but in consequence

of the exhaustion of the deposits of this substance it is gradually becoming less appreciated. Guano, which is the decomposed excrement of sea-birds, was found in large deposits on the Peruvian coast and the islands off that coast ; it is extremely rich in phosphoric acid and contains also much nitrogen.

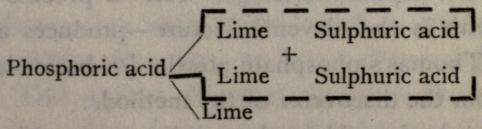
Finally, the dephosphorising of iron—a process which will be dealt with in the eleventh lecture—produces a substance known as Thomas's phosphate powder [or basic slag], a name derived from the discoverer of the method.

The phosphoric acid in these substances, with the exception of that in the material last mentioned and part of that in guano, is contained in the form of insoluble phosphate of lime, which is also the phosphate present in the soil.

When this insoluble phosphate is brought on to tilled land in fine powder its efficiency is very small, as it is very slowly broken up by the naturally occurring processes whereof we have spoken already. It is, indeed, almost valueless to the farmer, and the plants bring it into an available form only after the lapse of years. But matters are very different if this phosphate is artificially changed into a form which can be easily and readily assimilated by the roots of the plants. This process of decomposition consisted, until the year 1910, essentially in powdering the phosphate finely, and then treating it with concentrated sulphuric acid.

Most of the phosphoric acid in the materials we have mentioned is combined with lime, in the proportion of three molecules of lime to one molecule of the acid. Sulphuric acid is a stronger acid than phosphoric ; but one molecule of sulphuric acid combines with only one molecule of lime. If, then, two molecules of sulphuric acid are

caused to react with burnt bones, or mineral phosphorite, a new compound is obtained in which one molecule of phosphoric acid is combined with one molecule of lime, and at the same time two molecules of sulphate of lime, or *gypsum*, as it is commonly called, are formed. The following scheme makes the process more evident :



The phosphate of lime produced in this way is soluble in water, and is easily assimilated by plants when it is brought into the soil. It is sold under the name *superphosphate*. When one speaks of manuring with phosphoric acid one refers to this artificially prepared compound of phosphoric acid and lime. An aqueous solution of phosphoric acid itself is so corrosive that it would destroy all plant growth.

In order to make superphosphate it is necessary to use sulphuric acid, and this, of course, means expenditure of money. A cheaper method of making superphosphate has been sought for during the last fifty years. A process introduced in 1910 by a Norwegian named Palmaer for setting free the phosphoric acid in phosphorite seems to have become a serious competitor against the older method. Sodium chloride is the name given by chemists to common salt, because it is a compound of sodium and chlorine ; when an electric current is passed through an aqueous solution of this compound, under certain definite conditions, chlorate of soda is formed. (For some account of the chemical action of the electric current see Lectures IX. and XI.) Chlorate of soda can be separated by the current into soda and chloric acid, which can be kept apart. Phosphorite dissolves when it is

brought into the solution of chloric acid. If the soda is now added to this acid solution of phosphate of lime, the free acid is neutralised, and the phosphate of lime is thrown down as a fine powder, that is, in a condition eminently suited for use as a plant-manure. The liquid that is filtered from the precipitated phosphate contains only chlorate of soda. This liquid is again decomposed electrolytically, and the products —soda and chloric acid—are separated ; a fresh quantity of crude phosphorite is added to the chloric acid, and so the process is made continuous. The solution of chlorate of soda is used again and again for making fresh quantities of phosphate manure ; there is no waste of material except such loss as is inevitable in the process of manufacture. In place of the cost of sulphuric acid used in decomposing the crude phosphate, there is the smaller cost of the electrolytic plant ; not to mention other advantages which must be taken into account, such as the possibility of using phosphorite which could not profitably be treated by the older process, because of the impurities in it that would use up much sulphuric acid.

A word must still be said regarding the *Thomas's phosphate powder.* This substance contains a phosphate of lime which can be assimilated by plants without any preliminary treatment with sulphuric acid. As no money need be spent in artificially decomposing this substance, the Thomas's phosphate is a very cheap source of phosphoric acid ; it is much used for manuring meadow-land, for which purpose it is particularly suitable.

We come now to the consideration of potash salts as manuring material. Potash salts were very expensive until about the year 1860. Potashes, known in chemical language as carbonate of potash, was the only form in which potash

came into the market. As the name indicates, potashes was originally prepared by boiling plant-ashes with water in pots. It was much used in manufactures (glass making, soap making, dyeing, etc.); as the price was very high, and indeed continues high although it is now made from other salts of potash, it could never come into use as a material for manuring. In a later part of these lectures we shall consider this substance in more detail in connection with soda. All the other inexpensive potash salts in use to-day as manures are obtained from the salt mines in the neighbourhood of Stassfurt, near Magdeburg.

There were many salt-springs in Stassfurt that became exhausted during the last centuries. The exhaustion of these springs led to attempts to get rock-salt by boring in that neighbourhood. The boring brought up a kind of salt which tasted bitter; large quantities of this were thrown aside under the name of *Abraum salz* (useless salt), when pure rock-salt began to be obtained by mining.

These bitter salts are nothing else than salts of potash; and the immense deposits of such salts have caused a great industry to spring up in that neighbourhood whereby agriculturists all over the world are supplied with potash. It is necessary to work up the natural raw salts in manufactories in order to produce a material suitable for use as a manure. Some of the bye-products of this manufacture are also of technical importance.

It is supposed that these salt layers are the remains of a dried-up arm of a sea, which, after the first evaporation, repeatedly flowed over the deposits that had been formed, and in this way produced the great masses of salts that are found in the district.

Bromine is one of the things found in sea-water; this element was indeed first obtained from sea-water in

Southern France. Bromine plays an important part in photography, as we shall see later. Now the Stassfurt salts contain bromine, and the preparation of large quantities of this substance from these salts forms one of the minor industries carried on at Stassfurt.

We must now return to the consideration of the nitrogen that is required by plants. Plants require nitrogen for the building up of what is called vegetable albumen—we shall have to speak of this substance immediately when dealing with true albumen—a substance which conditions the life-functions of plants in a similar way to that wherein animal albumen acts. And so it is that want of nitrogen is synonymous with arrest of growth.

We did not find any nitrogen in the ashes of plants (see the analyses of plant-ash on p. 37), because compounds of nitrogen are not fixed in the fire, but are volatilised either unchanged or in combination with other elements; we considered the volatilisation of nitrogen in combination with hydrogen, as ammonia for instance, in dealing with the manufacture of coal-gas.

One would suppose at first sight that plants could never lack nitrogen; we know that the leaves of plants easily take the carbon the plants require from the air, and we also know that 10,000 parts of air contain only 3 parts of carbonic acid, whereas in the same quantity of air nearly 8,000 parts of nitrogen are present (see p. 8). But, as has been often said, nitrogen is a very indifferent gas, and most plants possess no arrangement for directly assimilating this inert material.

It is true that the air contains ammonia, which is a nitrogen compound soluble in water; but this substance is present in the air only in traces which must be reckoned

in parts per million. Now, as plants are not able to assimilate nitrogen compounds by their leaves, but only by their roots, it follows that, at most, only that part of this ammonia which circulates with the air in the soil, or that which percolates into the soil with the rain, can be available for the plants; and this quantity is quite insufficient to supply the nitrogen required by the plants.

Investigations made since 1886 have shown that certain bacilli play a very striking part in the process whereby plants assimilate nitrogen. There are certain bacilli in tilled soil which, while performing their vital processes, exhibit the remarkable property of causing the combination of nitrogen with oxygen. The compounds that are produced in this way react, in turn, with substances in the soil to form compounds that dissolve in water—chiefly salts of nitric acid—and these soluble compounds are then assimilated by plants. Nitric acid is a product of the oxidation of nitrogen; it is a compound of that element with oxygen and hydrogen.

Plants are known, belonging to the leguminous class, on whose root-nodules so much nitrogen-containing material is stored, in consequence of the activity of bacilli, that the soil is constantly rendered richer in nitrogen compounds by their growth; such plants are known as nitrogen-gatherers. If, then, plants whose roots do not possess this property are cultivated on a certain soil which has been sown the previous year with these nitrogen-gatherers, those plants find a store of material which supports their growth, although the soil has not been directly manured with nitrogen compounds. If this method of manuring is adopted the money value of the nitrogen may be taken as about 40 marks per hectare [about 16 shillings per acre], calculated on the present price of Chili saltpetre.

Attempts were made to apply these nitrogen-gathering

bacilli directly to soil-culture. The bacilli were bred in pure cultures which were brought into the market with the name *nitragin*. Before they were sown, the seeds were soaked in nitragin diluted with thin milk, so that the nitrogen-gathering bacilli adhered to each seed. The results of many experiments, made from the year 1896, have led to such unsatisfactory results that the method must be regarded as valueless to agriculture.

Now, before all this was known, experiments had shown that the addition to the soil of materials that contain nitrogen —or, as one may say, the assistance of the activity of the bacilli—was very beneficial to the growth of plants. Those nitrogen compounds which are soluble in water are of course the most efficient. There are four compounds which can be obtained in such quantities, and at so moderate a price, as to make them suitable to the agriculturist for this purpose.

One of these compounds is sulphate of ammonia; the second is Chili saltpetre; the third is calcium nitride; and the fourth is calcium nitrate. Until 1909, ammonia was obtained only from the gas-works. In its chemical relations ammonia is an alkali or a base, for these names have to-day the same meaning. The characteristic property of a base is that it is able to combine with acids; the product of such combination is called a salt. As there is an enormous number of acids and bases, so there is a very great number of salts related to these acids and bases.

Bases and acids may be gases, liquids, or solids. Ammonia, for instance, is a basic gas, aniline is a liquid base, carbonic acid is an acid gas, sulphuric acid is a liquid, and silicic acid is a solid. Silicic acid is regarded as an acid because it combines with bases to form silicates; for instance, with potash it forms silicate of potash. As ammonia gas is

very soluble in water, it is more convenient to use it in the form of an aqueous solution. Inasmuch as ammonia is commonly sold as an aqueous solution, it is often supposed that ammonia is a liquid.

Ammonia is used in agriculture in the form of sulphate of ammonia, which is a white solid formed by combining ammonia with sulphuric acid; this is found to be the most suitable compound of ammonia to use as a manure on the fields.

Nitre, or saltpetre, is the second source of nitrogen. This substance is produced by combining nitric acid with potash or soda; hence one speaks of potash saltpetre and soda saltpetre.*

Saltpetre has been known for long, and has been used in the manufacture of gunpowder. We shall have to consider gunpowder and the more recently introduced explosives when we have finished what we have to say about food-stuffs. Saltpetre is, however, too expensive for the farmer. The cheaper soda saltpetre is a discovery of our time. This salt is generally called Chili saltpetre, from the name of the country whence it comes. There are great stretches of land in Chili where rain never falls, and where therefore the soda saltpetre that is formed accumulates in the soil. The manufacture of soda saltpetre began about 1830; the process consists in lixiviating with water the soil that contains the salt, filtering, concentrating by evaporation, and then allowing the salt to crystallise out. The liquid which is drained off from

* Salts are called, ordinarily, by such names as *sulphate of potash*, *carbonate of soda*, etc., in accordance with older views of their constitution. Chemists now regard them somewhat differently, and speak of *potassium sulphate*, *sodium carbonate*, etc. The older names are retained in this book, as it is quite out of the question to go into the reason for the change.

the crystals is called the *mother-liquor*; this name is applied, in a general way, to any liquid from which crystals have separated.

When such mother-liquors are evaporated, the salts which were contained therein, in solution, separate out; salts obtained in this way are called mother-liquor salts. The mother-liquor from Chili saltpetre is not evaporated completely to dryness, because it is possible by partially evaporating this liquor to obtain the small quantities of the compounds of iodine which it contains. This comparatively rare element, iodine, is at present obtained chiefly from Chili. Experiments have shown that saltpetre provides plants with nitrogen more quickly and more thoroughly than any other nitrogen-manure.

The third source of nitrogen, calcium nitride, came into use in 1903. On p. 35 we learned something about calcium carbide. Professor Franck discovered that when nitrogen is passed over heated calcium carbide—and nitrogen can be cheaply obtained from the air (see p. 9)—a compound, calcium nitride, is formed. The first factory of calcium nitride was established, in 1905, by a Germany company, at Piano d'Orta in Italy, the site being chosen because of the cheap supply of power obtained from water. The yearly output of this factory is 80,000 centners (nearly 4,000 tons). A considerable amount of calcium nitride is now worked up into sulphate of ammonia, in the factories, and in this way the nitrogen of the atmosphere is made available for agriculture.

The problem of applying atmospheric nitrogen to agriculture was solved in quite a different way by Birkeland and Eyde. It had been known for long that traces of nitric acid were formed by passing electric sparks through moist air. The work of Birkeland and Eyde, and of many

other investigators since 1909, has so increased the yield of nitric acid that agriculturists have been able to buy nitric acid produced from the air, in the form of nitrate of calcium, at a sufficiently cheap price.

These two achievements of chemistry have caused the agriculture of the world for the first time to become independent of the supply of Chili saltpetre. The exhaustion of the deposits in Chili, which must have happened after about a century at the outside, would have made impossible the carrying on of agriculture on its present scale. The following table presents the average yield of wheat, in kilograms per hectare, in different countries, calculated on the average of the years 1905 to 1909. This table shows how the employment of artificial nitrogenous manures increases the yield in farming industries. [Kilogram per hectare divided by 125 is approximately equal to hundredweights per acre.]

	Kilos.		Kilos.
Great Britain ...	2,100	United States... ...	920
Germany	1,980	Spain	810
France	1,380	Argentine	770
Austria	1,320	Asiatic Russia ...	770
Canada	1,240	British Indies... ...	750
Hungary	1,200	Australia	670
Roumania	1,100	European Russia ...	670
Italy	1,030		

Now that we have become acquainted with the methods whereby plants are able to obtain everything they require for their growth from the inorganic world, including therein the air which surrounds us, let us pass on to consider the food of men and of animals.

Man is able to build up his body only from those organic substances which have already been put together by plants. For this purpose he makes use of fruit, grain, etc. ; but he can also use animals—oysters, for instance—or parts of animals,

such as their flesh. Animals themselves feed on plants or on other animals, so that the nourishment of the whole animal kingdom is derived primarily from the vegetable kingdom.

Everything which serves us as a food finds its way eventually into the stomach. Those constituents of food which are to be used for building up the body go into solution in the stomach and the intestines, and in this form they can be taken up by the blood, which carries to each part of the body what that part requires.

Let us carry out processes of digestion in several glass vessels by the aid of gastric juice. The coats of the stomach secrete a substance called *pepsin*, and the stomach, in its normal state, also contains a small quantity averaging about two-tenths of a per cent. of hydrochloric acid. These two substances, pepsin and hydrochloric acid, together are able to make soluble the undissolved albumens of the food ; or, as is generally said, to transform these albumens into *peptones*.

When a stomach is soaked in glycerin, the pepsin dissolves in the glycerin ; in our experiment we shall employ such a solution of pepsin in glycerin. The experiment is made in the following simple manner.

We heat a chamber, which can be closed, to about 37° C. [98·5° F.], which is approximately the temperature of the body, and we place four glasses containing a little water in the warm chamber. In one of these glasses we place some of our pepsin solution, into another we pour hydrochloric acid, and into the third and fourth we put both pepsin and hydrochloric acid. As the substance to be digested we choose *fibrin* (about which albuminoid substance we shall learn more hereafter) and some hard-boiled white of eggs. We put both of these substances into the first and second glasses, and only

one of them into each of the third and fourth glasses (see fig. 16).

The process of dissolving albumen is not a chemical reaction in the ordinary meaning of that term, and it does not take place instantaneously, as so many chemical reactions do. As about half an hour must elapse before a noticeable quantity of the albumen has dissolved, we shall allow the experiment to proceed, and come back to it again at the end of the lecture, when we shall be able to convince ourselves that the desired result has been obtained.

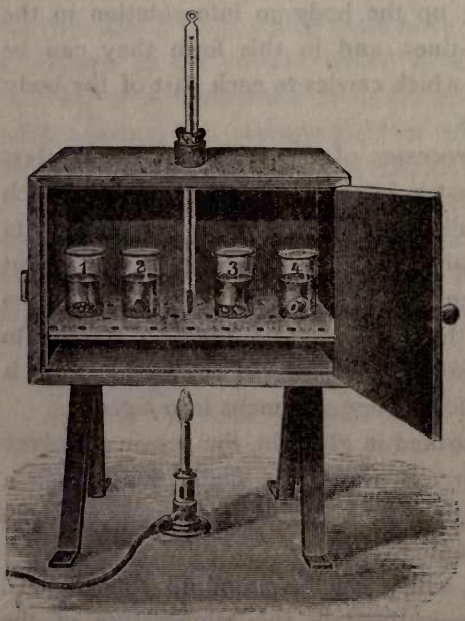


Fig. 16.

The active substance in the stomach, which, as we know, is called pepsin, is only active in the presence of acids; but the substance called *trypsin*, which causes digestion in the intestines, is effective only in the presence of alkali; the contents of the intestines, therefore, show an alkaline reaction.

It is easy to understand that, when substances are got into solution in these ways, such substances pass into the blood, and are carried through the whole of the body. But there are other questions which press for answers, but which no one has as yet succeeded in answering.

We have taken for granted, as self-evident, that processes of digestion go on in the stomach. But the stomach itself consists of flesh—namely, of albuminoid substances; why, then, does not the stomach digest itself? how can it resist the action of the digesting fluid? We digest a goose's stomach with readiness; and if you ascribe part of the digestibility to the process of cooking, you must remember that such an animal as a dog is able to digest an uncooked goose's stomach without trouble.

No certain answer has yet been found to the question we have proposed. We know that the secretion of the stomach is acid, and that the blood shows an alkaline reaction; and we may suppose that the acid and the alkali neutralise one another in the coats of the stomach, and that the process of digestion is thus put an end to. But we cannot decide at present whether this is or is not the actual reason of the durability of the stomach.

There are many other unexplained problems connected with the process of digestion. Not to be tedious, let us select only one of these. Where does the stomach get the intelligence which enables it to select from the food all those things that are required by the body as a whole? We may very well suppose that the stomach looks after itself, and takes what it requires for its own sustenance from the food-stuffs that come into it. But how does the stomach know what quantity of phosphate of lime the bones require for their existence, and what the brain requires? How does the whole digestive apparatus find out how much nourishment must be given to the blood to keep up the increase of the body till the twenty-second year, and no longer?

But we are coming nearer to the difficult problems of

physiological chemistry, and that is a domain into which we cannot enter here.

To be frank, we cannot say exactly what hunger or thirst is. One man feels hunger more in his throat, another more in his stomach. Nature has, however, taken care that when hunger assails us we should know that this disagreeable sensation can be removed by taking food ; and as regards the choice of food she has left us plenty of room for selection.

Looked at chemically, food materials may be divided into three main classes : the albuminoids (in addition to gelatin) ; the fats ; and the carbohydrates (starch and sugar).

The albuminoids are substances which contain nitrogen ; their composition is very complicated. They are formed, naturally, in plants (see p. 59), whence they find their way, with other food-stuffs, into the animal body. Other, very complicated, albuminoid substances are built up from these in the animal body ; and having performed their proper functions, they finally leave the body, in the urine, in the form of a substance called *urea*, which is extremely rich in nitrogen and has a comparatively simple composition. It is easy to calculate the quantity of albuminoids which a man has used, for his existence, in 24 hours, by determining the amount of nitrogen in the urine passed in that time.

The name *albuminoids* is derived from egg-albumen ; but in the course of time it has received a very wide connotation, which we have already more accurately defined, and has come to be applied both to albumen-like bodies which are soluble, and to similar bodies which are insoluble, in water. The albuminoids which are soluble in water—the albumen of eggs, for instance—are coagulated by boiling. This change is a very remarkable one. At any rate, there is not another

of the many substances that have been made artificially by chemists in the course of time which exhibits this property.

The most important albuminoid of milk, which is called *casein*, is not coagulated by boiling ; but if the slightest trace of acid be present in the milk the casein separates out in flakes. This separation is made visible to you when I add a few drops of vinegar to some milk. Milk goes sour, apparently spontaneously, in warm, summer weather, and curdles whether you will or not. The reason of this souring is as follows. Besides containing about 3 per cent. of casein, milk also contains more than 4 per cent. of a sugar called *milk-sugar* ; this sugar, like most other sugars, can ferment—that is to say, it can be transformed under definite conditions into other substances—without a specific chemical action.

The following table shows the average composition of milk and of cream :

	Milk.	Cream.
Water	87·70	68·82
Casein	2·91	3·76
Albumen soluble in water	0·52	
Fat	3·32	22·66
Milk-sugar	4·84	4·23
Ash	0·71	0·53

No fermentation can occur without the presence of certain organisms—fungi, or bacilli, as they are called to-day ; these are everywhere in the air, but they are active only under certain suitable conditions. The lactic acid bacillus, which is so called because it changes milk-sugar into lactic acid—we shall meet with this organism more than once in the course of these lectures—begins to act on milk at a temperature between 20° and 30° [68° and 86° F.] ; milk therefore curdles, by the formation in it of lactic acid, only on warm days.

When milk curdles by souring, casein separates from it. Milk can also be curdled intentionally by means of rennet; and the substance which separates is used as a food-stuff, after being properly manipulated, and is called cheese. Rennet is a ferment analogous to pepsin; this ferment is not, however, present in all stomachs, but it is found especially in the mucous membrane of the fourth stomach of the calf. Because of the importance of milk as a nourishing food for children, many attempts have been made to preserve this liquid for a lengthened period—in other words, to prevent it from going sour. Soxhlet's apparatus is now used in many families for this purpose. In this process, milk is heated for some time in a closed flask to 100° C. [212° F.]; all the bacilli in the milk are thus killed, and also all other bacteria which might bring about putrefaction. As long as the vessel is kept firmly closed, bacilli cannot fall into the milk from the air, and hence souring, curdling, and putrefaction cannot occur.

However, milk which has been boiled in this apparatus is not quite the same as unboiled milk. The casein, the fat, the milk-sugar, etc., are unchanged; but that portion of the albuminoids, other than casein, which is soluble in water—and which amounts (see table, p. 57) to about one-sixth of the total albuminoids—is coagulated by the continued boiling, and is thus made more difficult to digest. It is customary nowadays to employ a more convenient form of apparatus for boiling milk, which, although it does not insure the absolute security of Soxhlet's method, is found to be more suitable for preparing milk for children's use, provided it is used with reasonable care.

Besides those albuminoids which coagulate, some by heat and some by addition of acids, there are other substances

of this class which remain dissolved as long as they are in a living body, but solidify very soon after they are withdrawn therefrom. Substances of this kind exist in blood ; and when blood is exposed to the air it soon separates into a solid and a liquid portion. The solid, red mass becomes colourless when it is washed with water, and the washed substance is called *fibrin*. It was fibrin that we employed in our experiments on digestion, because this substance has been found to be readily peptonised when digested artificially, and hence it is very suitable for such a lecture experiment.

The liquid which remains when fibrin is separated from blood is called *blood-serum*. Since 1894, serum from the blood of animals has been used as a curative agent in several diseases that are caused by bacilli ; for instance, in diphtheria. When diphtheria-bacilli grow in a suitable liquid they produce a virulent poison ; by filtering off the bacilli, a liquid is obtained, the quantity of poison in which cannot increase, because the poison-producing bacilli have been removed. If a moderate amount of this liquid is injected under the skin of an animal, the poison in the liquid acts on the animal, which soon sickens ; but at the same time an antidote to the poison is produced. By repeating the injections, the antidote accumulates in the serum of the animal, and such serum is used as a curative agent in cases of diphtheria.

We shall not go deeper into the very difficult subject of the classification of the albuminoids. It should be noted that, speaking chemically, flesh belongs to the albuminoids, inasmuch as it is a very complex aggregate of nitrogen-containing substances.

One thing only is to be remarked. Albuminoids occur in the vegetable kingdom ; wheat-meal contains about 10 per cent., grass from 2 to 3 per cent., and hay from 10 to 12 per cent. of albuminoids. Dried potatoes—dried

in a heating apparatus—contain about 6 per cent. of albuminoids.

It is customary nowadays for farmers to buy artificial fodder when they have not raised a sufficient quantity of natural fodder for their cattle; on account of their great nourishing power such artificial fodders are known as feeding-stuffs. Most of these feeding-stuffs consist of the cakes that remain when the oil is pressed out of certain plant-seeds which are rich in that substance; [hence the name *oil-cake*]. These substances are remarkable for the large quantity of albuminoids they contain; this may amount to 50 per cent., as, for instance, in cakes made from the seeds of the sun-flower. In order to avoid the application of the term albumen to a constituent of plant-seeds, which may seem somewhat strange to ordinary ears, it is customary to speak of these substances as *proteïds*, a nomenclature which was introduced into the chemistry of the albuminoids in the forties of last century.

Let us now see what are the results of our experiments on digestion (see p. 54). Looking at the contents of the first and second glasses, we see that neither the fibrin nor the hard-boiled egg-albumen has been at all changed by digestion with pepsin only; that the fibrin has been caused to swell up, but has not been dissolved, by the hydrochloric acid only; while the acid has produced no change in the hard-boiled egg-albumen. Now, looking at the contents of the third and fourth glasses, we see that the mixture of pepsin and hydrochloric acid has so acted on the fibrin that that substance has gone entirely into solution; if we examine this solution more narrowly we shall find that the fibrin has been changed into a peptone, which, as we know, is a soluble albuminoid. The hard-boiled white of eggs, if not dissolved and changed into

peptones, has certainly been much acted on by the mixture of pepsin and hydrochloric acid. This substance is not so easily digested as fibrin; had we allowed the experiment to continue for a longer time we should have got the whole of the egg-white into solution.

In actual digestion things will of course proceed in a similar way. Hard white of eggs is rightly regarded as not easy to digest; but although the process of digestion occupies more time in this than in some other cases—than, for instance, in the digestion of flesh—hard-boiled eggs are not harmful to a healthy stomach, but they are not to be recommended when one's stomach is out of order.

The albuminoids are exceedingly complicated substances, chemically considered; the process of digestion converts them into peptones. In recent years, Fischer, professor in Berlin, has succeeded in preparing peptone-like bodies in the laboratory. This work is the most remarkable which has yet been done in the domain of scientific chemistry; the further development of the labours of the talented investigator is awaited by the scientific world with the greatest attention.

Before leaving the albuminoids we must just glance at the substance called *gelatin*. The cartilage, the bones, and all the ligatures of the animal body contain substances which dissolve in water when boiled therewith for some time and form a liquid which gelatinises as it cools. Gelatin is obtained by drying such gelatinised solutions. As thus prepared, gelatin is used as a glue.

Gelatin contains a large quantity of nitrogen. The following analyses show that the percentage of nitrogen in this substance does not differ much from that in the more characteristic albuminoids: gelatin may, indeed, to some extent be substituted for albumen in foods, in some of which

—for instance, in that prepared by boiling bones—it is contained along with albumen; it is also found in soups and sauces.

	Egg-Albumen.	Plant Albumen from Wheat.	Gelatin.
Carbon	52·25	54·3	50·1
Hydrogen	6·90	7·2	7·5
Nitrogen	15·25	16·2	17·5
Sulphur	1·93	1·0	—
Oxygen	23·67	21·3	24·9
	100·00	100·0	100·0

LECTURE IV

Mixed diet—Butter—Margarine—Starch—The sugars—Ripening of fruits—The diet of diabetic patients—Fruit-sugar—Bonbons—Burnt sugar as a colouring material—Cane sugar—Saccharin—The absorption of food—Common salt—Iron—Importance of cooking—Soups—Bread making—Boiling potatoes.

THE albumen which is consumed in food serves to replace that which is used in carrying on the vital functions of the body. But other kinds of nourishment besides albuminoid substances are required to supply the energy which the body constantly requires, for instance, for moving itself as a whole, or for moving parts of itself—say for continuing the action of the heart—and also for constantly maintaining the temperature of the body, by the burning of carbon finally to carbonic acid, at that degree which is necessary for the proper performance of the bodily functions.

The simple replacement of the carbonic acid which is expired in the breath (see p. 10), for instance, does not require the presence of any nitrogenous food, as carbonic acid is composed of carbon and oxygen only.

Now we know that nature has given us a fairly wide choice in the matter of food-materials, and the quantity of carbon in a diet very rich in nitrogen may suffice for all the needs of the animal body. This is proved by the case of beasts of prey, some of whom consume only flesh, which has been

shown, by experiment, to contain extremely little non-nitrogenous food-materials, to be, indeed, an almost purely albuminoid food.

A pure albuminoid diet is certainly not required for the proper maintenance of the body; we much prefer a mixed diet—that is to say, we take various dishes in the course of a day, which dishes contain sufficient albumen to make up for what is used in the body, and also sufficient non-nitrogenous nourishment to carry on the work of the body and to maintain the bodily temperature; and we supply our want of liquids by adding water or some liquid form of nourishment.

The non-nitrogenous food-stuffs belong to two chief classes —the fats and the carbohydrates. As the fats and the carbohydrates do not contain nitrogen, these substances take their place among the food-stuffs by virtue of the carbon which they contain. Fats are formed chiefly in animals, but to some extent also in plants; plant-fats are generally called oils by those who are not chemists. On the other hand, all the carbohydrates which are used as foods come from the vegetable kingdom.

The fact, so often noted with astonishment by travellers, that the Greenlanders consume large quantities of blubber and fat, will readily be understood from what has been said. As these people cannot till the fields, and therefore can have neither meal nor sugar, etc., for consumption, they are obliged to supply all their needs in the way of non-nitrogenous food by consuming the one kind of such food—fat—which they can get. We enjoy both kinds of non-nitrogenous foods. We consume fats in the form of fat or butter, and carbohydrates in the form of bread (or other preparation of flour), potatoes, and the like. In more southern latitudes plant-fats, such as

olive oil, are used as foods. Man has known instinctively how to obtain fats and carbohydrates from his surroundings.

A very large part of the fats consumed in our latitudes is consumed in the form of butter, which is made from milk. When milk is allowed to stand it gradually separates into two layers, the lighter fat-globules floating upwards and forming the cream, and the milk, deprived of fats—or the skim milk—remaining below. When the cream is violently agitated, as is done in churning, the single fat-globules gather together and become solid, and so form butter.

The somewhat high price of butter led to attempts to fabricate an artificial substitute. These attempts were successful in France about the year 1870. This substitute for butter was made until a few years ago from ox-tallow. The tallow is melted ; the liquid is completely separated from pieces of skin by filtration ; the clear liquid is mixed with a little salt, and is allowed to stand for twenty-four hours at the temperature of 25° C. [77° F.] whereby it is partially solidified, after which it is pressed in an apparatus kept at 25° C. The residue in the presses, which consists chiefly of stearate of glycerin, is used for making stearin candles (see p. 19), while that which flows from the presses comes into the market under the name of *oleomargarine*. If oleomargarine is to be made into artificial butter there is added about a third of its weight of cotton-seed oil and earth-nut oil, and it is then mixed with about half its weight of cows' milk, and about the same quantity of water is added. By vigorous beating this mixture is caused to separate gradually into two parts, one of which is the artificial butter, and the other is an aqueous liquid. Sweet milk is used for the better sorts, and skim milk for the cheaper kinds, of artificial butter.

The fat which is left in fresh animal flesh by the butcher is

most generally used for making artificial butter; and after that, preference is given to the fat of pigs, large quantities of which are sent into the market from North America.

Let us now consider the carbohydrates.

The name *carbohydrates* is derived from the proportion in which the elementary constituents of these substances are contained in them. This class of bodies includes starch powders, the sugars, and other similar substances with which we shall become acquainted in another lecture. The sugar which is found in grapes, and which is generally known as *grape sugar*, has the following composition, stated in atoms:

GRAPE SUGAR.

6	atoms of carbon	(represented by the letter	C).
12	„ hydrogen	(„ „ „	H).
6	„ oxygen	(„ „ „	O).

Using the contractions already explained (see p. 23), this composition is expressed by the formula

$$C_6H_{12}O_6.$$

The proportion of the atoms of hydrogen to the atoms of oxygen is as 2 is to 1, which is the same as the proportion of the atoms of these elements in water whose formula is H_2O.

It used to be supposed that these substances were composed of carbon united with water; hence the name *carbohydrate* was given to all of them, for in all the proportion of the hydrogen atoms to the atoms of oxygen is as 2 is to 1.

Very remarkable researches, which were brought towards completion only in the last years of the nineteenth century, have shown that the conclusion drawn from the analytical results—namely, that those substances are compounds of carbon and water—is not justifiable. The name carbohydrate is therefore quite inapplicable; nevertheless, it is retained as a convenient general designation for this class of compounds.

Starch, which is a most important carbohydrate, is found everywhere in the vegetable kingdom. The chlorophyll-containing granules of leaves are able to make use of the carbonic acid of the air for building up starch (see p. 36). Starch, therefore, is found in all the green parts of leaves. This substance, starch, at last accumulates in those organs of plants which serve as storers of reserve material (see p. 99). We find these especially in the bulbs and roots, in the fruit, and in the seeds.

Whatever be the source of the starch, the composition of it is always expressed by the chemical formula $C_6H_{10}O_5$; but the granules of starch obtained from different plants show noticeable differences when looked at under the microscope.

Starch is generally prepared from potatoes, wheat, rice, or maize. The process consists, in the main, in rasping the potatoes, etc., along with water, and passing the product through fine sieves; the coarser parts remain on the sieves, while the starch granules pass through the meshes in suspension in water.

The turbid liquid that is obtained in this way is allowed to settle in barrels, and the starch gradually falls to the bottom. The liquid is drawn off, the deposited starch is drained, and finally dried at a temperature which must not be too high, as if moist starch is heated to about 50° or 60° C. [120° to 140° F.] it is completely changed, its structure disappears, and it becomes what we call paste.

Starch is spoken of as potato-starch, wheat-starch, etc., according to the name of the plant from which it has been obtained. Starches which come from foreign countries are generally called by special names, such as *arrowroot*, which is obtained from the roots of various tropical plants, and different specimens of which are not identical.

Sago-starch is somewhat different from these other starches.

It is obtained from the pith of certain palms by grinding in the same way as potato-starch is made. After being completely dried the substance is allowed to fall through sieves on to warm metallic plates. This causes a partial conversion into paste of the exterior parts of the granules, and these gather together into little round balls that are sent into the market under the name of *sago*.

The following analyses show the quantities of starch and other constituents in the seeds and tubers that are most commonly consumed. The analyses represent the composition of ground corn, as it is only in this form that the grains of wheat, rye, etc., are used as foods.

		Finest Wheat-meal.	Rye-meal, mean composition.	Potatoes, mean composition.	
	Water	14·86	15·06	75·48	per cent.
	Albuminoids	8·91	11·52	1·95	„
	Fats	1·16	1·79	0·15	„
Carbohydrates.	**Starch ... ...**	**65·93**	**62·00**	**20·69**	„
	Sugar	2·23	0·95	—	„
	Gum and Dextrin ...	6·03	4·86	—	„
	Cellulose	0·33	2·11	0·75	„
	Ash	0·55	1·71	0·98	„
		100·00	100·00	100·00	„

Bran, that is the husks of the grain which do not pass through the sieves wherein the grain is shaken after grinding, is used as fodder for cattle. Analyses of bran give the following results :

	Wheat-bran.	Rye-bran.	
Water	13·2	12·5	per cent.
Albuminoids	14·1	14·5	„
Fats	3·7	3·4	„
Carbohydrates	56·0	59·0	„
Cellulose	7·2	6·0	„
Ash	5·8	4·6	„
	100·0	100·0	„

Bran is richer in albuminoids than flour ; hence, bread made with the husks as well as the grain of wheat and rye is very nourishing. The appearance and taste of such bread are often objected to.

These analyses show a certain amount of *cellulose* in wheat, rye-meal, potatoes, and bran ; this substance is a carbohydrate, and its composition is expressed by the formula $C_6H_{10}O_5$; but as it is quite indigestible, it does not represent any nutritive element.

We must now proceed to the consideration of the sugars. Although a great many kinds of sugar are found in nature, yet the varieties of sugar are much less numerous than the different kinds of starch. Starches and sugars are nearly related to one another, and starches are converted into sugars, especially into grape sugars, with the greatest ease.

We may often notice this change taking place in ordinary life. Unripe fruits have not a sweet taste ; but some of them —for instance, strawberries—acquire this taste in a few hours. The cause of this process is to be found in the change of a portion of the starch contained in the strawberries into sugar. This change occurs not only when the fruit ripens, but it may also be brought about by cooling the fruit below 0° C. [32° F.]. For instance, we know that the taste of potatoes which have been frozen is sweet, although not altogether agreeable. The cause is the same in both cases.

The rapid conversion of starch into sugar may be demonstrated by adding powdered starch to some water that contains a little acid, say hydrochloric acid, and boiling for a short time ; a portion of the starch is thus converted into sugar, and the presence of sugar may be shown by making use of the following chemical reaction. If we add caustic

soda and copper sulphate (blue vitriol) to some water we get a bluish precipitate of copper hydroxide ; and if we now boil for a little time, this bluish precipitate is changed into black oxide of copper. The presence of starch does not alter this reaction ; but if we boil some starch with a little hydrochloric acid, and then add caustic soda and a solution of copper sulphate to this liquid, we do not obtain a blue precipitate, but a sky-blue liquid ; if we now boil this blue liquid there is formed in it, not a black, but a red, precipitate of cuprous oxide (protoxide of copper). This reaction is characteristic of grape sugar.*

The sugar that is produced in this way from starch is grape sugar. The chemical process is easily understood. That starch may be changed into sugar it is only necessary for the starch to combine with the elements of water. Thus,

Starch, which consists of	takes up water, which consists of	and produces grape sugar, which consists of
6 atoms of carbon		6 atoms of carbon
10 atoms of hydrogen	2 atoms of hydrogen	12 atoms of hydrogen
5 atoms of oxygen	1 atom of oxygen	6 atoms of oxygen

The change may be represented more shortly in this way :

$$\underset{\text{Starch.}}{C_6H_{10}O_5} + \underset{\text{Water.}}{H_2O} = \underset{\text{Grape-sugar.}}{C_6H_{12}O_6}$$

* When this reaction is applied to urine it enables the practitioner to diagnose diabetes, as diabetic patients excrete grape sugar.

From what we now know it is easy to understand the reason for the special diet which is prescribed to such patients. Except in the most advanced stages of diabetes, when all the material transformations that normally occur in the body are thrown into complete disorder (and such changes we shall not of course consider here), albumen cannot be changed into sugar; there is also no intimate chemical connection between fats and sugar ; but we have just convinced ourselves that starch and sugar are very closely related. If, then, a diabetic patient is

There are certain substances which stand between starch and grape sugar; the best known of these is *dextrin*, which can be prepared, among other ways, by heating starch to 170°—200° C. [340°—390° F.]. Dextrin is much used as a substitute for gum arabic.

Grape sugar is manufactured by boiling starch with acids, and is sent into the market under the name of starch-sugar, or more generally, *glucose*. As it is very difficult to cause this sugar to crystallise, even when working in the laboratory on a small scale, commercial glucose presents the form of a syrup. This syrup forms a passable substitute for honey. It is much used for the preparation of gingerbread biscuits; but its chief application is in the making of *bonbons*, as when these are made by using glucose they are not so hard as if cane sugar were employed.

Glucose is also employed for making sugar-colouring. If one heats a little glucose in a glass vessel till it becomes dark brown, allows it to cool, and then adds some water, the colour changes to the yellowish brown tint of cognac; on further standing the colour deepens and becomes that of dark coloured beer, although, as we shall learn hereafter, the colour of such beer is not produced in this way.

As this sugar-colouring is quite harmless, it is very useful for colouring articles of food or confectionery.

put on a diet of albuminoids and fats—if he consume flesh, eggs, butter, and the like—he will not excrete any sugar. But if he is allowed to consume dishes prepared from meals or potatoes, or such vegetable products, all of which contain much starch, these will give rise to the excretion of greater or smaller quantities of sugar; he should therefore be bidden to abstain from such foods as far as he possibly can.

In the less serious stages of the disease the use of certain quantities of starchy foods may be valuable for the general nourishment of the body of the patient, and for this reason he may be allowed to consume a little, but only a little, wheaten or rye bread, etc.

Cane sugar, which is used by us every day and comes as a sweetening into every meal, is of more interest to us than glucose, which we only occasionally see as such in our ordinary way of living. Before the introduction of cane sugar honey was the only sweetening material; and it is very doubtful whether we should now be pleased with the sweetened dishes, tasting of honey, which the ancient Romans set before their guests at their feasts, or with those honeyed preparations that were consumed in the earlier Middle Ages in the patrician houses of Nürnberg.

As its name implies, cane sugar is the produce of a cane-like plant; it is got from the sugar-cane. This plant grows only in Southern climates; the knowledge of it was brought to Europe by the Crusaders. At first the sweet juice of the plant was used in the form of a syrup; the preparation of the solid sugar dates from the year 1400. About one hundred years later began the process of refining cane sugar, by dissolving the crude sugar in water, clearing the solution, and allowing the much purer sugar to crystallise out, after boiling.

As soon as cane sugar had become an easily transported article of commerce the manufacture of it advanced rapidly, and the sugar-cane began to be cultivated in every country where the climate allowed of its growth. The plant was introduced into Central America, especially into the West Indies, about 1500; and after about six years so much sugar was manufactured there, by the labour of slaves shipped from Africa, that the cultivation of the cane almost ceased in other parts of the world, even in the East Indies where the climate was well suited for this purpose. The plant was introduced at an early date into Sicily by the victorious Arabians; and that island is the most northern country where the cultivation has been attempted. But the industry has disappeared from

Sicily, and from Europe in general, since the American over-production began.

In 1747 the Berlin chemist Marggraf discovered that the same sugar which is obtained from the sugar-cane exists in beetroots. This discovery was of the greatest importance to European agriculture, as it introduced a new, and for a long time very profitable, crop.

Marggraf was perfectly conscious of the far-reaching character of his discovery. A kinsman of his, named Achard, very soon endeavoured to manufacture sugar from beetroots on a large scale, on his land at Kaulsdorf, near Berlin, but without success, because the cheap colonial sugar made it impossible to run a paying factory in Europe at that time. But the state of affairs was altered by political changes. In consequence of the Continental blockade of the first Napoleon, the price of all colonial productions which had until then been imported into Europe by the English rose immensely, and this was especially true of sugar, the price of which rose to four shillings per pound. Under these conditions the manufacture of beetroot sugar was bound to be a paying business, and this business was eagerly undertaken.

The raising of the Continental blockade ruined most of the sugar factories then in work; but so much experience had been amassed in the manufacture that at last this sugar gained a firm hold on the market in opposition to the colonial sugar, especially as the latter, being a very convenient object of taxation, was obliged to pay a high import duty.

The manufacture of sugar from beetroots has in the course of years become an enormous concern, and it has been brought to great perfection by the combined action of science and industry. The following figures make this very evident.

To obtain 100 lbs. of sugar there were required—

In the year	1836	...	...	...	...	1,800 lbs. of beetroot.
„	1842	...	...	...	...	1,600 „ „
„	1857	...	...	...	...	1,200 „ „
„	1871	...	...	...	...	1,100 „ ,
„	1900	...	...	...	...	750 „ „

Marggraf found that the beetroots cultivated in his time contained rather more than 6 per cent. of sugar. The percentage has been raised since then by the proper choice of roots and manures. An average of 14 per cent. was obtained in 1890, and about 18 per cent. in 1910.

Until the year 1900 the production of beet sugar increased much more rapidly than that of cane sugar. The following table gives some data :—

	Production in tons = 1000 kilograms.			Percentage of Beet sugar produced.
Year.	Cane Sugar.	Beet Sugar.	Total.	
1840	1,100,000	50,000	1,150,000	4·35
1880	1,852,000	1,402,000	3,254,000	43·08
1890	2,069,000	3,633,000	5,702,000	63·70
1900	2,862,000	5,575,000	8,437,000	65·08
1910	8,170,000	6,510,000	14,680,000	44·33

The manufacture of cane sugar has increased more rapidly than that of beet sugar since 1900. In Germany, at present, the maximum quantity of sugar obtained from the beets grown on one hectare of land is 5,000 kilograms (in 1870 it was 2,000 kilograms); the intelligent Dutch sugar growers in Java obtain as much as 15,000 kilograms of sugar from the sugar-cane grown on a hectare of land.

In order to extract the sugar the beetroots are first of all crushed and rasped to a pulp, and all the sugar is then removed by treatment for several hours in what is called a *battery of diffusers*. The juice must then be evaporated,

This process presents many difficulties, because if sugar-syrup is boiled for a long time the sugar is altered and becomes non-crystallisable. But the difficulties have been overcome by carrying on the evaporation of the sugar solution under a greatly reduced pressure, instead of in open vessels as in ordinary processes of boiling down; the syrup boils at a much lower temperature in an evacuated vessel than it would do in an open vessel. In the first lecture we had ocular demonstration of the pressure of the air (see p. 3). Suppose water is heated; before the vapour of the water can rise freely—that is, before the water can boil—the pressure of this vapour upwards must be sufficient to overcome the downward pressure of the atmosphere. Now if the air is removed from a closed vessel—say from a copper vessel, such as is used in the sugar factory—by means of an air-pump, the vapour of water in such a vessel will ascend much more easily than if the water were in an open vessel; and therefore water will boil in such a vessel at a temperature much lower than its ordinary boiling-point, which is 100° C. [212° F.].

The process may perhaps be more easily understood by considering the following fact. Water boils on the top of Mont Blanc at 85° C. [185° F.], because the height of the column of air which presses on the surface of the water is as much less than that of the air-column at the level of the sea as is the height of the top of the mountain above the sea-level.

The sugar-juice can be boiled down without any danger at the greatly reduced temperature obtained by using an apparatus from which most of the air has been removed. After sufficient evaporation and cooling, sugar separates from the liquid in crystals, which are then purified and sent into the market in the form of sugar-loaves. Animal

charcoal (see p. 42) is made use of for effecting the complete decolourisation of the syrup.

The mother-liquor (see p. 51) from crystallised sugar is known as *molasses*. For a long time no method could be found for obtaining the sugar that remained in this liquid, but, by methods suggested by chemists about the year 1882, the whole of the sugar can now be withdrawn from molasses. Large quantities of molasses are now used as fodder for cows; the molasses are mixed with finely chopped straw, preferably with straw from rape plants.

In connection with the sugars it will be well to say a word on the most recently introduced sweetening material, called *saccharin*, a name derived from *saccharum*, the Latin word for sugar.

Of the vast number of chemical compounds there are certain to be many with a pronounced taste; the acids, for instance, take their name from the fact that the earliest discovered substances of this class had an acid taste. Bases such as potash or soda have a caustic, soap-like taste. Some salts, that is compounds of acids and bases, have a pure salt-like taste, others a bitter taste, and some are tasteless. The tastes of the many compounds which do not belong to one or other of these three classes are almost infinitely varied. Omitting sugar, a few substances with a somewhat sweetish taste, such as *alanine*, have been known for long. But it happens that only one substance has been discovered, up till now, which is so extraordinarily sweet that one part of it is equal in sweetening power to 300 parts of sugar: this substance is saccharin. The chemical composition of saccharin is very complex; its systematic chemical name is *sulpho-benzimide*.

Saccharin has no value as a food, quite independently of

the fact that it is never consumed except in very minute quantities. It may be used for sweetening all sorts of things; but it has proved beneficial chiefly to patients suffering from diabetes, who are able by its help to enjoy the sweet taste of dishes which they were obliged wholly to renounce before the discovery of saccharin.

The advantages of sweetening dishes in this way should not be regarded as small, inasmuch as many foods are thus made more easy of consumption. For there is no doubt that emotional conditions, as well as physical needs, play a part in the absorption of foods. We continue to take only such means of nourishment as have been made agreeable to our palates in one way or another. It appears as if such condiments as salt, pepper, and mustard were required to rouse the digestive processes into activity. Indeed, we go further than this; we regularly enjoy warm decoctions of coffee or tea, the nourishing value of which is *nil*, because we know by experience that these make easier the consumption of solid nourishment.

Spirituous drinks occupy a position between those things we consume for nourishment and those we consume for pleasure; and when we go more into detail we shall find that these liquids belong more to the latter than to the former class.

Experience teaches us that men fairly easily get accustomed to one kind of delicacy or beverage, so that the continued use of the same thing either leads to satiety, or the wished-for effect can be obtained only by increasing the quantity, with the result that excess is indulged in, and deplorable consequences follow. Hence it follows that there must be a considerable variety of dishes in a diet which is suitable for constant use, and that a careful selection must be made

of the condiments which are added to give flavour and agreeableness to the dishes. Happily experience and daily habit have taught most housewives how to insure this result.

Refinement of cooking is by no means an improper object of endeavour. It is certainly as permissible as thousands of those other attempts after enjoyment which seek to make life more pleasant. By this we do not mean to advocate the consumption of dinners with an interminable array of different courses, but only to assert that the housewife does well when she takes care that what is put on the table is so prepared that it may be agreeable and may be consumed with pleasure.

It should not be overlooked that the preparation of food-stuffs on a large scale brings many advantages with it. In towns every one has his bread from the baker, and so he gets it fresh every day and with a good flavour; but in those country parts where each household must do its own baking the bread is generally stale, because it is impossible to prepare every day just what is wanted for the day's consumption. No one would assert that to bring about an improvement in the quality of bread for general consumption would be either wasteful or luxurious.

The preserved vegetables, which make it possible to enjoy vegetable diet in winter almost as cheaply as in summer, and also those preparations of meat and fish which are much used nowadays, belong to the substances we are now considering. Such things enable one to vary one's meals at a very small cost.

The well-known saying, "*toujours perdrix*," shows very forcibly that a thing which in itself is extremely good eating, and when taken occasionally is peculiarly pleasurable to the palate, becomes altogether unenjoyable when consumed constantly for a long time.

It is not only human beings who object to monotony in diet; flesh-eating animals do the same. Rats certainly soon die if they can get nothing but boiled flesh; after a time they refuse to touch it, and prefer to starve rather than to eat the flesh. Birds seem to differ in this respect from flesh-eaters, as they may be fed in captivity for years on the same kind of grain or seed without taking any hurt.

The analyses given on p. 68 of corn-grains certainly show us that these taken alone represent a mixed diet, and this may be the reason why they can be used as food for a long time.

To maintain life we require water and certain inorganic salts, besides albuminoids, fats, and carbohydrates. The only inorganic salt which we use directly in our food is common salt, which is a substance that we add intentionally to most dishes, and a substance which seems to have a specific beneficial effect on the animal body. We notice that where opportunity serves many animals resort eagerly and regularly to salt deposits.

The analyses of food-stuffs that have been given—and those which are to follow—show that the other salts which we require, such, for instance, as phosphate of lime for the bones, are contained in sufficient quantities in our ordinary foods. The total quantity of these salts is represented as ashes in the analyses. Iron is the only one of these inorganic substances which possesses much interest when a general survey is being made of the subject.

The quantity of iron required daily by a human being is extremely small; it may be taken as one-seventh of a milligram per kilo. of body-weight [about $\frac{1}{1000}$ of a grain per lb.]. This amounts to only about 3 grams per year for a person weighing 50 kilo. [about 45 grains for a person of 8 stone

weight]; nevertheless, it is well known that an insufficient absorption of iron leads to *chlorosis* and to many subsequent disorders. When one is in health the requisite quantity of iron is quite provided for by the food consumed; but in certain ailments, such as chlorosis in young girls, the power of the organism to assimilate iron from the food is so reduced that iron must be supplied artificially if the requisite absorption of that substance is to take place. It is often very difficult to find the proper iron tonic, because these medicines affect different individuals in very different ways. For this reason, new preparations of iron are constantly making their appearance. This at least can be asserted to-day, that the power of iron compounds, taken as medicines, to increase the formation of blood is an incontestable fact which is no longer disputed by any physician. The quantities of iron and of chalk in different food-stuffs are given in the following table, for the especial reason that these numbers deal with a matter which is of great interest to many people.

The numbers given below are taken from determinations made in 1904:

	Milligrams in 100 grams.		Grains in 1 lb.	
	Iron.	Chalk.	Iron.	Chalk.
Sugar	—	—	—	—
Egg-albumen ...	—	18·8	—	1·33
Cherries	0·24	27·2	0·017	1·93
Women's Milk ...	0·28 to 0·37	29·2	0·02 to 0·026	2·07
Cow's Milk ...	0·30	196·3	0·021	13·94
Apples	0·30	10·6	0·021	0·75
Rice	0·88 to 2·2	90·6	0·06 to 0·15	6·43
White Bread ...	0·96	29·5	0·071	20·8
Asparagus ...	1·20	—	0·08	—
Potatoes	1·60	25·0	0·11	1·77
Rye	3·2 to 4·2	52·7 to 62·4	0·23 to 0·30	3·74 to 4·43
Spinach	4 to 4·7	—	0·29 to 0·33	—
Beef	4·7	8·1	0·33	0.57
Wheat	4·84	56·6	0.34	4·0
Egg-yolks ...	5 to 11·9	189	0·35 to 0·84	13·4

The quantity of iron in yolk of eggs varies with the time of year; it is greatest at the period of hatching.

Now that we have considered separately the classes of substances that are required for the nourishment of our bodies we must deal with the dietetic value of cooking. Animal and vegetable food-stuffs differ much when looked at in this respect. The preparation of animal flesh is not very important so far as the nourishing value of the flesh is concerned. Raw minced beef-steak, made palatable by the addition of pepper and salt, is generally thought to be very nourishing, and this supposition is not unjustified. We certainly cannot enjoy the raw flesh of fish or birds; nevertheless the nourishing value of such flesh is not altered by boiling or frying. In the process of frying, however, the heating of the flesh with fat produces substances that have a pleasant odour and an appetising flavour, and which therefore make the consumption of the food easier. The five following analyses will elucidate what has been said:

	Water.	Proteïds.	Fats.	Extractive substances.	Ash.
Fresh beef contains	70·88	22·51	4·52	0·86	1·23
After boiling it contains ...	56·82	34·13	7·50	0·40	1·15
Cooked beef-steak contains ...	55·39	34·23	8·21	0·72	1·45
Uncooked veal cutlets contain...	71·55	20·24	6·38	0·68	1·15
Cooked veal cutlets contain ...	57·59	29·00	11·55	0·43	1·43

What especially strikes us in these analyses is that boiled beef contains less water than uncooked beef. This decrease in the quantity of water is due to the shrinking of the fibres of the beef brought about by the heating. But it is much more remarkable that the composition of boiled beef, or, as we may call it, soup-beef, should be so nearly the same as that of beef-steak; the percentage of albuminoids (proteïds) is indeed the same in both. There is, however, a difference in

the quantities of extractive substances; in beefsteak these substances are nearly double what they are in boiled beef. In these analyses *extractive substances* mean those substances, other than albuminoids and fats, which go into solution when the meat is boiled with water. Now these are just the substances that have an appetising effect on the palate. Such cooked foods as soup-beef, which contain but little of these extractives, taste insipid, and are not eaten with pleasure. Soup-beef, however, falls but little behind other kinds of animal food in respect of nourishing value; hence, if it is not overboiled, and eaten with condiments that make it more palatable, it is not to be despised.

And this brings us to inquire as to the best way of proceeding when soup is to be made from meat. Ought the meat to be put into cold water, or into hot water? Let us answer the question by an experiment.

We cover some minced beef with cold water and shake thoroughly—the beef is minced so that a large surface may be exposed to the action of the water. We now filter off the solid matter, and thus obtain a clear liquid coloured reddish by the presence of a small quantity of the colouring matters of blood. On now pouring this liquid into a beaker glass and boiling, we notice that its colour changes to grey—as the colouring matter of blood is unstable when heated—and that a great deal of a flocculent solid, which is found by experiment to be albumen, separates from the liquid. The cold water has thus withdrawn some soluble albumen from the meat, and this has of course coagulated when the liquid was boiled. Now when soup is skimmed the albumen which has become solid by boiling is removed in the scum, and so this amount of nourishment is sacrificed to the better appearance of the soup.

Now let us pour boiling water over another portion of the minced beef, and then boil for a short time. The meat very soon becomes grey, inasmuch as the colouring matter of blood cannot withstand the heat. We notice but few flocks of albumen floating in the liquid, and if we pour the liquid through a filter we obtain a clear fluid which does not become turbid when it is boiled.

In the latter part of this experiment the boiling water brought about the coagulation of the particles of albumen on the surface of the meat; the fine pores of the meat were thus stopped up, and but very little of the extractive substances found their way into the water.

The results of everyday experience confirm our experiment. If one wants to make a very well flavoured soup, the meat must be put into cold water, because much extractive matter will thus be taken out of the meat; the meat that remains will, however, be disagreeably tasted: but if one wishes to get palatable meat hot water must be used; in this case the flavour of the soup will not be very good.

Generally speaking soups are required to be pleasant to the palate, rather than to possess a high nutritive value; the results of the analysis of a soup, prepared in the ordinary way from 500 grams [about 1 lb.] of beef and 190 grams [about $\frac{2}{5}$ lb.] of veal bones, will show that this requirement is fulfilled.

Water	95·18 per cent.
Proteïds	1·19 „ „
Fats	1·48 „ „
Extractive substances	1·83 „ „
Ash	0·32 „ „

Water is the chief constituent of this soup. The proteïds consist chiefly of gelatin, as the albuminoids have been coagulated by the heating and removed by skimming. The

quantity of fat is of course inconsiderable. Still we consume soups willingly, and experience teaches us to ascribe to them a stimulating action on the nervous system ; this action must be regarded as due to the extractives, and also to the potash salts, they contain. About half of the ash of the soup referred to in the foregoing analysis consisted of potash, and about one-fourth of phosphoric acid. The addition of herbs to soups serves of course only to improve the flavour.

The importance of boiling, baking, etc., is very different in the case of vegetable foods from what it is when animal food is concerned. Most vegetable substances, except fruits, are too hard to be eaten uncooked, and their organised tissues, to which they owe their existence, must be broken up by cooking before we can use them as foods.

The different kinds of grains, which are the chief sources of our vegetable foods, must be broken up and freed from their husks by grinding in order that we may get at the flour within. But even then the flour is not suitable for human food, as the raw starch granules surrounded by their cell-coverings are only very slowly attacked by the digestive fluids. Quite a different state of affairs is brought about by heating the flour with water; the coverings of the cells are burst open, the starch escapes and passes into the pasty condition, when it is easily digested (see p. 67). The same purpose is served by the baking of bread, which process also brings about that peculiar sponginess of texture to which bread owes its great digestibility.

When flour is stirred up with water a very tough dough is obtained, because of the *gluten* in the flour. Gluten is a proteïd substance contained in flour which becomes of a glue-like consistence (hence the name) when moistened. If such dough is baked without further treatment a hard mass is obtained

somewhat resembling ship biscuits. But if the dough is allowed to stand for some time it undergoes change; yeast-cells fall into it from the air, and these cause the sugar of the flour to ferment (a process to be dealt with immediately); the bacilli which cause lactic fermentation (see p. 57) also find their way into the dough, and produce lactic acid from the sugar. The lactic acid—and other acids chemically like it which are also produced in the dough—then acts on the starch to produce glucose, so that, even if the flour originally contained but little sugar, the yeast finds sufficient sugar to ferment.

Fermentation caused by yeast, by which process all spirituous drinks (to be considered in detail in the next lecture) are prepared, consists in the transformation of sugar (glucose) into carbonic acid gas and spirit, or, as the latter substance is called in chemistry, *alcohol*. The process may be represented as follows:

One molecule of grape sugar, consisting of	produces two molecules of alcohol, each consisting of	and two molecules of carbonic acid, each consisting of
6 atoms of carbon	2 atoms of carbon	1 atom of carbon
12 atoms of hydrogen	6 atoms of hydrogen	
6 atoms of oxygen	1 atom of oxygen	2 atoms of oxygen.

The process is presented more shortly thus:

$C_6H_{12}O_6$	=	$2\ C_2H_6O$	+	$2\ CO_2$.
1 molecule glucose	=	2 mols. alcohol		2 mols. carbonic acid.

One molecule of sugar (glucose) is transformed into two molecules of alcohol and two of carbonic acid gas. The carbonic acid gas is produced in the dough, and, as it cannot escape from the pasty mass, it causes the dough to *rise*—that is, to swell up in bubbles. When the dough is put into the oven the alcohol begins to evaporate, and this process also tends to loosen the bread and make it spongy. The heat

also breaks up the cells of the moist starch granules which at once begin to become pasty. The outer portions of the bread become so hot that, when the bread is sufficiently baked, part of the starch is converted into dextrin (see p. 71); and as dextrin has a somewhat pasty consistence, the starch granules, and other similar constituents of the bread, adhere together and form the crust that we are accustomed to see on the outside of loaves of bread.

If bread dough is allowed to stand in the air it becomes sour because of the formation in it of lactic acid and other similar acids.

It takes a considerable time for dough to ferment and become sour by the action of the yeast cells and bacilli that may fall into it from the air; but if fresh dough is mixed with a little dough that has become sour by standing in the air fermentation processes go on rapidly, as it is known that yeast cells and bacilli increase in number with extraordinary rapidity. When therefore one batch of dough has fermented, a small quantity of it is set aside in order to start the fermentative changes in the next batch. The flavour of sour dough is communicated to bread baked with such dough. Nowadays only black bread is made with sour dough, and the peculiar flavour of this bread is due to the dough used in making it. For making white bread it is preferred to use fresh yeast; this yeast was formerly obtained from the breweries, but to-day it is prepared for baking purposes by a special process. We shall leave the further consideration of this subject until we are speaking of fermented drinks, when we shall have a better grasp of the facts that are needed for its elucidation.

There are several substances which are used as substitutes for yeast in causing dough to rise. Carbonate of ammonia is sometimes used in household baking, under the name of

salts of hartshorn. This substance is composed of ammonia, which is a basic gas, and carbonic acid, which is an acid gas (see p. 49); the substance is a solid, but at the temperature of the baking oven it is resolved into its gaseous constituents, and these gases cause the dough to rise. Potashes, which is carbonate of potash (see p. 45), is also used. The solid salt is not decomposed by heat, but it gives off carbonic acid gas if it is mixed with sour dough. If the dough contains lactic acid this acid decomposes the carbonate of potash, forming lactate of potash, and carbonic acid gas which permeates the dough and causes it to rise. The action of this salt is effectual only when dough contains a considerable quantity of acid, for only then is sufficient carbonic acid gas produced to bring about the proper rising of the dough.

Reflection will show that the process of raising dough by fermentation must be accompanied by the loss of some nutritive substances, because fermentation always means destruction of sugar. Following Liebig, attempts have been made to obviate this loss by using baking powders whereby sufficient carbonic acid should be produced in the dough to cause it to rise and to become spongy.

Horsford's baking powder, for instance, which is much used, is a mixture of bicarbonate of soda and acid phosphate of lime; when this is kneaded into dough, the moisture in the dough induces a reaction between the constituents of the baking powder whereby carbonic acid gas is produced in such quantity that the dough becomes loose and spongy and ready for putting into the baking oven. Another baking powder consists of a mixture of tartaric acid and carbonate of soda with powdered starch. The action of this powder is similar to that of Horsford's powder; the starch is quite superfluous.

It remains now to say a word or two on the boiling of

potatoes. Raw potatoes are much too hard to be consumed as food. Their hardness is caused by the husks which enclose the starch granules; these husks are so connected together as to form what may be called the skeleton of the potato. This skeleton is so compact that the starch granules cannot be disintegrated by the digestive fluids in the human stomach. But when potatoes are boiled the husks are burst off from the starch granules, and these granules assimilate water and pass into that pasty state wherein the digestive fluids readily act on them with the production of sugar (see p. 69). The sugar thus finds its way into the system, and is used for nourishing the body.

It will be easy for you to apply the principles laid down and illustrated in this lecture to the boiling and baking, etc., of other kinds of food-stuffs besides those we have especially mentioned here.

LECTURE V

Quantity of food that must be consumed, and nutritive values of the chief foods—Fermentation—Wine—Cider and perry—Champagne—Mead—Koumiss—Beer—Malt—Spirits—Dry yeast [German yeast]—Brandy—Potato spirit—Vinasse—Spirit refining—Absolute alcohol—Methylated alcohol—Liqueurs.

WE come now to the important question, how much must a man eat to keep himself in full vigour? We know already that he ought to consume a mixed diet, consisting of both nitrogenous substances (albuminoids) and non-nitrogenous substances (fats and carbohydrates).

The greater or less abstinence of the vegetarians cannot make us forget this aspect of the question of food. As these people reject all albuminoids which are of animal origin, they must derive the nitrogenous food which they require altogether from plants. The analyses which have been put before you (p. 68) show that the proportion of the two kinds of food in plants is unsuitable, inasmuch as the quantity of carbohydrates so greatly preponderates that if sufficient albuminoid substances are to be obtained from that source it is necessary to take into the body at the same time far more than enough useless ballast in the form of carbohydrates. Of course it may be demonstrated that a man can exist on vegetable diet only. But the argument that such graminivorous animals as the horse or the elephant become very vigorous on a purely vegetable diet is not to the point, because nature has

provided such animals with very long intestines for the better absorption of this diet. Many graminivorous animals have also several stomachs, and they masticate their food repeatedly.

While it is possible for the vegetarian to feed himself sufficiently by this method without too much trouble, it seems that a purely albuminoid diet can scarcely suffice for the nourishment of human beings. This is made evident in the cases of diabetic patients; such people ought not to consume anything of vegetable origin, but it is impossible for them to continue such a diet for a length of time. The almost total denial to them of food containing starchy matter is a source of lasting discomfort, and yet this is the only way of preventing those serious consequences which are otherwise certainly induced by this disease.

Many investigations have been carried out by Voit and Pettenkofer with regard to the quantity of nourishment that is required by a man daily. We shall quote a few of the results.

An efficient worker requires daily, when he is working,

137 grams [about 2,100 grains] albumen, 173 grams [about 2,650 grains] fats, and 352 grams [about 5,400 grains] carbohydrates (starch or sugar).

The following numbers were brought out in the case of a young physician:

127 grams [about 1,950 grains] albumen, 89 grams [about 1,370 grains] fats, and 362 grams [about 5,600 grains] carbohydrates.

The following numbers represent mean values:

118 grams [about 1,800 grains] albumen, 88·4 grams [about 1,360 grains] fats, and 392·3 grams [about 6,040 grains] carbohydrates.

This quantity of albumen corresponds to 18·3 grams [about

282 grains] nitrogen, which is the quantity contained in the following weights of different food-stuffs:

	Grams	= Lbs.		Grams	= Lbs.
Cheese ...	272	0·6	Cream ...	2,650	8·4
Peas ...	520	1·15	Milk	2,905	6·4
Lean flesh	538	1·18	Potatoes ...	4,575	10·1
Wheat flour	796	1·75	Bacon	4,796	10·57
Eggs * ...	905	2	White Cabbage	7,625	16·8
Black Bread	1,430	3·15	Beer	17,000	37·5
Rice ...	1,868	4·12			

The amount of carbon required daily by a man is 328 grams [about 5,050 grains]; this quantity is contained in the following weights of different food-stuffs:

	Grams	= Lbs.		Grams	= Lbs.
Bacon ...	450	0·99	Eggs	2,231	4·91
Wheat flour	824	1·81	Lean flesh ...	2,620	5·77
Rice ...	896	1·97	Potatoes ...	3,124	6·89
Peas ...	919	2·03	Milk	4,652	10·25
Cheese ...	1,160	2·56	White Cabbage	9,318	20·54
Black Bread	1,346	2·97	Beer	13,160	29·01
Cream ...	1,410	3·13			

If we weigh out the quantity of carbon that our daily need demands, say in the form of wood charcoal, we are astonished to find that more carbon is required for twenty-four hours' heating of a man—if one may use such an expression—than for heating a small stove during the same time. It requires much more carbon than we generally suppose to maintain a human body—weighing, say, 70 kilos. [about 11 stones]—constantly at the temperature of 37° C. [98·5° F.] and to keep it in vigour. If we think of the human body as a machine,

* A question is often asked as to the relative nutritive values of eggs and meat; the numbers in the tables show that, on an average, from 18 to 20 eggs are equal to 1 kilo. [about 2¼ lbs.] of meat.

we must remember that, like the bodies of other animals, it differs from ordinary machines in that the substance of all the organs is constantly changing, whereas the material of a machine remains unchanged.

If the foregoing numbers are examined more closely they are found to confirm the ordinary experience of life for the most part, but in some particulars they go against our preconceived opinions. A diet of bacon and peas is generally thought to be very nourishing, and our tables show that we need not consume very much of these two together to supply our daily requirements. But if we desire to obtain sufficient nourishment from beer alone, the tables show that the nutritive value of this drink is so small that 17 litres [$3\frac{3}{4}$ gallons] of it are required to furnish sufficient albuminoid substances, and 13 litres [2 gallons] to furnish sufficient carbon for a day's requirements. Beer indeed can scarcely be called a food in the strict sense of that term; it must rather be regarded as a nourishing beverage, for the regular consumption of, say, a litre [$1\frac{3}{4}$ pints] of beer per day will supply only about one-seventeenth of the total nourishment that we require.

Black, or rye, bread is the most perfect of all the foods mentioned in the preceding tables, for about $1\frac{1}{2}$ kilos. [$3\frac{1}{3}$ lbs.] of that substance suffice to supply the total daily needs of a man. This explains the fact that labourers are very vigorous, although they are not so well nourished as the better-to-do classes, who regularly eat meat. It is also easy to understand that, because of the constant use of his muscular activity, a labourer may possess a greater physical energy than those who are much better off in so far as change of diet is concerned.

The numbers which have been given exhibit the minimum

quantities of nourishment required for the maintenance of the life of a man in full work. If any one falls below this he gradually collapses; even those who are especially abstemious must consume at least this minimum quantity. Generally speaking a man eats much more than this, as it is quite impossible to maintain the theoretically correct proportion of the different kinds of food, and, moreover, habit plays a very important part in the matter.

The body assimilates what it requires for its existence, and what remains unused is excreted.

The statement we have made that a man can exist on 1½ kilos. [3⅓ lbs.] of rye bread consumed daily is of course purely theoretical, inasmuch as no one is able to live on rye bread alone for a length of time. But if the bread is made more palatable by the addition of butter, sausages, or the like, and if some other food is substituted every day for part of the bread, such a beverage as warm coffee being also consumed, then the statement expresses what actually happens with many people.

Let us now consider fermented liquors more fully than we did in the last lecture.

If liquids that contain sugar, but not very large quantities of sugar, are exposed to the air they slowly undergo a very marked change in their properties, and this change is accompanied by the evolution of gas and the formation of a deposit which is known by the name of *yeast*.

The most striking feature of the change is that the liquids have become intoxicating. The process itself is known as *fermentation*, and the liquids that are produced are called fermented liquors.

Very concentrated sugar solutions do not undergo this process; such liquids have indeed preservative properties, and

these properties are taken advantage of in the preparation of preserved fruit.*

It has already been pointed out (p. 57) that all processes of fermentation are caused by exceedingly minute living organisms which are present everywhere in the air. That organism which especially causes the change of sugar into alcohol and carbonic acid is called *Saccharomyces cerevisiæ*.†

The juice obtained by pressing grapes—called *must*—is the most easily fermented of all liquids. This juice contains the directly fermentable sugar, *glucose*, and also all those substances which yeast requires for its growth; for as yeast is a living organism it can only thrive under definite conditions—for instance, in the presence of certain inorganic salts.

The liquid which is finally obtained by this fermentation is called *wine*.

We can tell from their flavour that wines made from different kinds of grapes contain very different quantities of sugar; the quantity of alcohol in wines also varies, the upper limit being determined by the fact that when the quantity in a fermenting liquid reaches about 16 per cent. by volume the yeast dies. The following table, however, shows that some wines contain much more than 16 per cent. of alcohol by volume. To such wines alcohol has been added. The addition of alcohol is made partly for the purpose of making the

* It should be noted that some sugars do not undergo fermentation, and that cane sugar and milk sugar belong to those which cannot be fermented directly. But when fermentation is set up in substances contained in a solution in which these sugars are present the sugars themselves are changed into fermentable sugars (see forward).

† We are not concerned here with a purely chemical reaction, but with changes that are connected with the life-processes of certain moulds; small quantities of other substances besides the main products are formed in these changes.

wine keep better, and partly to give that particular flavour which the public are accustomed to connect with the name of the wine in question.

	Alcohol. Volume per cent.	Sugar. Per cent.
Silesian wine	5·5	—
Markobrunner (1882)	7·17	—
Liebfraumilch (1875)...	11·55	—
Vöslauer Goldeck (1868)	10·28	—
St. Julien (1865)	9·28	—
Chablis (1862)...	9·30	—
Malmsey	7·50	36·40
Samos	14·96	7·68
Tokay, selected	10·76	25·34
Tokay, selected II.	14·84	8·20
Port	19·82	4·82
Madeira	19·12	3·46
Malaga...	15·12	15·50
Sherry	21·22	2·04

This table, which is made somewhat lengthy because of the many different kinds of wine we meet with, shows that the sugar in wines made from very sweet grapes is not wholly converted into alcohol, for the reason already mentioned, while there is no sugar in wines that are made from grapes poor in sugar. The sugarless wines are suitable for diabetic patients.

That fine aroma, which always becomes more apparent as wines age, called the bouquet of wines, is due to chemical compounds, all of which cannot be accurately defined, but among which are to be found certain *ethereal salts of organic acids*, a class of compounds the composition of which cannot be explained without a more profound chemical knowledge. These compounds are formed in wines by the agency of bacteria. Small quantities of bacteria have been found in wines kept in corked bottles for as long as forty years.

Cider and perry are alcoholic liquids prepared by pressing apples and pears and allowing the musts to ferment. As the juices of these fruits contain but little sugar the liquid obtained by the fermentation of these juices would be very poor in alcohol; sugar is therefore added to the musts before fermentation begins, and a proper amount of the most important constituent is thus insured in the fermented products. When currants or similar slightly sweet fruits are made use of, the addition of sugar is absolutely necessary if a drink is to be obtained with anything like a fair amount of alcohol in it.

Beverages free from alcohol are now prepared in considerable quantities, by boiling the peelings of apples with water—the apple-peelings are imported for the most part from America, where they are dried before being shipped—and impregnating the liquid with carbonic acid gas.

Champagne is prepared from grape-musts in many countries. The name is derived from the district of *Champagne*, where this wine has been prepared certainly since the middle of the eighteenth century.* Champagne is made by pouring the must, after the first energetic fermentation is over, into bottles, which are then tightly corked. As the after-fermentation proceeds carbonic acid gas is generated, and as this gas cannot escape it gradually produces a considerable pressure inside the bottles. As many impurities are gradually deposited while the wine is fermenting in the bottles, the custom is to set the bottles on their heads as the second fermentation is proceeding, and to give them a twisting movement from time to time; a work-

* The word *sack* [*sekt* in German], which is so often used by Falstaff, means what we now call sherry. The actor Devrient brought the word *sekt* into fashion [in Germany] as a name for champagne about the year 1820

man then opens the bottle, and the first portion of liquid that is driven out carries these impurities with it. The bottles are then turned round, filled up with the *liqueur*, and corked. The bottles are kept for some time before they are sent into the market. When the wire that holds the cork is removed the accumulated carbonic acid forces out the cork with a loud sound.

The composition of the liqueurs on which the flavour of the finished wine so much depends is kept secret by the manufacturers.

In former days about one-fourth of the bottles were broken during the manufacture by the great outward pressure of the carbonic acid; but the glass industry is so much improved that not more than one bottle in a hundred bursts nowadays.

It is evident that wherever wine is made champagne might be manufactured; but the minute carefulness required in the processes must always prevent good champagne from becoming cheap, as we see in the prices of the best brands. Notwithstanding this we know that effervescing wines can be bought to-day at a very low price; but these liquors are not made in the same way as champagne, and indeed they have nothing in common with genuine champagne except the name. The manufacture consists in forcing carbonic acid—in the same way as is practised in making soda water—into light white wines which have been sweetened, if necessary, by adding sugar; when this is done the champagne is ready for the market.

A bottle of soda water can be bought to-day for a few pence; hence to charge wine with carbonic acid, and so to change it into so-called champagne, can cost but little, and the product can be sold very cheaply.

While the inhabitants of countries where the vine flourishes

have been acquainted with wine since the earliest times, because its preparation almost forced itself on their notice, people living in more northern climes found other methods for obtaining alcoholic liquors, the use of which when once acquired seems never to have been abandoned by any race.

The dwellers in the lands north of the Alps, where the vine was introduced when these countries were conquered by the Romans, were long ago acquainted with *mead*. This drink is easily made; the starting-point is honey, which is very rich in sugar. The honey of bees does not ferment of itself because it is too concentrated; but if it is diluted, and exposed to air, fermentation is brought about by the yeast which falls into it, and the intoxicating liquor called mead is produced. To-day this drink is as good as forgotten; its taste, as one may easily convince oneself, is not very agreeable.

The drinking of *koumiss*, which is fermented mares' milk, has probably persisted since early days; but this drink is found only in Central Asia, whence it has never spread. We must say a little about the production of this drink, because when milk stands in the air in our climate it is not changed by yeast into an intoxicating liquid, but it becomes sour by the conversion of its sugar into lactic acid through the agency of the lactic ferment (see p. 5).

If milk is diluted with about ten times its volume of water, and some koumiss is then added to the diluted milk, the lactic ferment in the koumiss quickly causes the conversion of a part of the milk-sugar into lactic acid, and this acid then reacts with the rest of the milk-sugar and transforms that into a sugar which is directly fermentable (see the footnote, p. 94), and then fermentation into alcohol and carbonic acid begins.

Cows' milk can be converted into an intoxicating liquor by a similar process ; and the preparation of this liquid has been attempted in many places on a large scale, but the manufacture has been given up, as the taste of the drink does not seem to suit the palates of Europeans.

People living in European countries where the vine will not flourish have learnt, in the course of time, to manufacture beer in place of mead and similar drinks ; and the taste of beer is so much better than that of the last-mentioned alcoholic liquids that beer has driven these entirely out of use.

The preparation of beer rests on the following principles. When seeds are placed in moist earth they soon put forth rootlets and then leaves. The rootlets are not, however, at once able to carry nourishment to the leaves, and so the supplies of starch flour and albumen stored in the seeds are drawn upon. As germination proceeds a substance is formed which converts the starch into sugar and dextrin, and the albuminoids at the same time become soluble. The substances held in reserve in the seeds having thus become soluble serve to nourish the plantlet until the roots have strengthened sufficiently to take this duty on themselves.

Experience has shown that barley grains are the most suitable of all cereals for beer making, the proper understanding of which process requires us to bear in mind what has just been said. Certain kinds of beer—Berlin *Weissbier*, for instance—can be made from wheat.

We shall confine our attention to beer made from barley, as that beer is much more generally consumed than any other, and it will then be easy to understand the preparation of other kinds of beer.

For the purpose of making beer barley is steeped in water and is then placed in a cellar kept not too cold. The result is that the barley germinates without being put into the earth; little roots are pushed forth, and the substance—called *diastase*—which has the property of changing starch into sugar, is formed in the barley. The albuminoids in the barley at the same time become soluble in water.

When the rootlets have grown as much as experience has shown to be proper the barley is dried, and the substance so obtained is called *malt*. The drying may be done in an open place, but it is generally carried out by maltsters in kilns—that is, in highly heated apartments. The higher the temperature employed in the kilns the greater is the quantity of brown substances produced in the malt, and therefore the darker is the colour of the beer. If very dark-coloured beer is to be made a portion of the malt is finally roasted in an apparatus like a coffee-roaster (cf. p. 71).

The malt is now crushed, and it is then run into tuns, where it is treated with water kept at 50° to 70° C. [120° to 170° F.], because the conversion of starch into sugar and dextrin proceeds most rapidly at this temperature. The liquor obtained by this process of *mashing* is called *wort*; it contains much sugar. But if this liquor were fermented without any other treatment a very disagreeable beer would be obtained. It has long been known that if a drink with a pleasant flavour is to be obtained from malt some bitter substance must be added. Hops are used everywhere for this purpose; they have been grown on the Rhine since the ninth century. Oak wood was used at one time in some parts of Germany for imparting a bitter flavour to beer; but such beer would not find favour nowadays.

The wort is boiled with hops; in this process some water is evaporated, and the wort thus becomes slightly more

concentrated. The wort is now cooled by exposure in flat vessels, the process being hastened by mechanical contrivances. If the cooling is not done rapidly there is a danger of the fermentation proceeding in a wrong direction ; for the lactic fermentation, that we have often spoken of, is liable to begin between 25° and 30° C. [77° and 86° F.], and if this occurs the beer is spoilt. The last process consists in allowing the liquid, cooled to the proper temperature, to ferment in large vats, after some yeast taken from a former fermentation has been added to it.

If the liquid were allowed to stand until sufficient yeast had fallen into it from the air the process of fermentation would be very slow and very uncertain ; but if some yeast is added this yeast very quickly grows in the liquid, inasmuch as it finds there everything that is required for its nourishment. If the fermentation is allowed to proceed at a temperature of 12° to 15° C. [53° to 59° F.] the production of carbonic acid is so rapid that the bubbles of this gas carry yeast cells with them to the surface of the fermenting liquid. The beer produced in this way is called *high fermentation beer*; the flavour of such beer is not cared for [in Germany]. [English beer is generally made by high fermentation, the fermentative process being started at about 60° F. and carried up to 70° F. or more.]

In Bavarian breweries fermentation is carried on at from 6° to 8° C. [43° to 46½° F.] ; the process goes on very slowly, and, as bubbles of carbonic acid form very gradually and rise one by one to the surface, the yeast sinks to the bottoms of the vessels. The product is called *low fermentation beer*; it keeps well, and its flavour is so excellent that it is sent all over the world, and wins golden opinions everywhere. But to make beer drinkable it must be charged with carbonic acid gas, else it is flat and insipid. In order to charge it

with the required quantity of carbonic acid the fermented liquor is placed in barrels, where a very slow but continuous secondary fermentation proceeds. The bungs are placed in these barrels a short time before the beer is to be drunk, and the carbonic acid, which continues to be produced but cannot now escape, gradually accumulates in the beer. The amount of carbonic acid produced in this final process does not exceed about two-tenths of a per cent.

The following analyses show the quantities of the more important constituents in those beers which are in most demand; the numbers given are the mean results of many analyses:

	Water.	Carbonic acid.	Alcohol percentage by weight.	Sugar.	Ash.
Draught or winter beer ...	91·81	0·228	3·206	0·442	0·20
Lager, or summer beer ...	90·71	0·218	3·679	0·872	0·223
Pale beer (*Weissbier*) ...	91·64	0·279	2·510	—	0·163
Porter	87·10	0·155	5·350	1·340	0·419
[Burton ale...	79·6		5·90		
Scotch ale	80·45		8·50]		

We must now consider spirits and the liquors prepared from spirits.

Although the intoxicating effect of wine was known very long ago, yet it was not till the eighth century that the intoxicating principle was separated from wine; the separation was effected by the Arabians after they had discovered the process of distillation.*

* To conduct a distillation seems to us a very simple process; yet in the days of antiquity, although people were much interested in nature, this method of separating a volatile liquid from a less volatile or a non-volatile substance was never employed. The ancients were more inclined towards that kind of natural philosophy which expected to answer all questions by speculative thought rather than to the genuine scientific investigation of nature by means of experiment.

It was known in ancient days that new and useful compounds could be obtained from various substances by what we should to-day call distilla-

When wine is distilled a clear, colourless, agreeably smelling liquid passes over, the most striking property of which liquid is its combustibility. This distillate was named *alcohol* by the Arabians. As this liquid seemed to be the spirit, or essence, of the wine it was called at a later time *spiritus vini.* The residue, with which nothing could be done, was called *phlegm*; hence Schiller's saying, "*Zum Teufel ist der Spiritus, das Phlegma ist geblieben.*"

As we are dealing at present with fermented liquors we will convince ourselves that there is a substance in beer, as well as in wine, which can be volatilised by boiling, and is combustible. Experiments have proved that the substance obtained in this way from beer is the same as that got from wine—that, indeed, it is alcohol.

We pour the contents of a bottle of beer into a flask, into which we then fit a cork carrying a glass tube about a metre

tions. For instance, Pliny tells that an oil can be obtained from turpentine, which is a resin that exudes from many trees when their bark is cut, by boiling the turpentine with water in vessels over which woollen cloths are suspended, and then pressing these cloths; and uses for this oil must have been known, as it was prepared in considerable quantities. But no one hit on the idea of distilling turpentine resin in order to obtain an oil (what we now call turpentine oil), and the exceedingly incomplete method of getting the oil described by Pliny remained in use.

It may not be without interest to mention that camphor is obtained to-day by the inhabitants of the island of Formosa by a method the same as that described by Pliny two thousand years ago for making an oil from turpentine resin. The Formosans boil the wood of the camphor tree with water in vessels over which they place deep lids filled inside with brushwood. The camphor is volatilised with the steam (some of which of course escapes) and then, by reason of the partial cooling, solidifies on the brushwood in little pellets; the yield of camphor is equal to about 3 per cent. of the quantity of wood used. The purification of camphor by sublimation, whereby it assumes the appearance that is familiar to us, is conducted in Europe.

and a half [almost 5 feet] long (see fig. 17). We now cause the beer to boil freely, and at the same time we bring a lighted taper to the opening of the glass tube; the alcohol vapour that is rising from the tube takes fire and burns with a long flame. The flame soon goes out, as there is but a small quantity of alcohol in a bottle of beer; nevertheless we have in this way, so to say, directly burned out the alcohol from the beer.

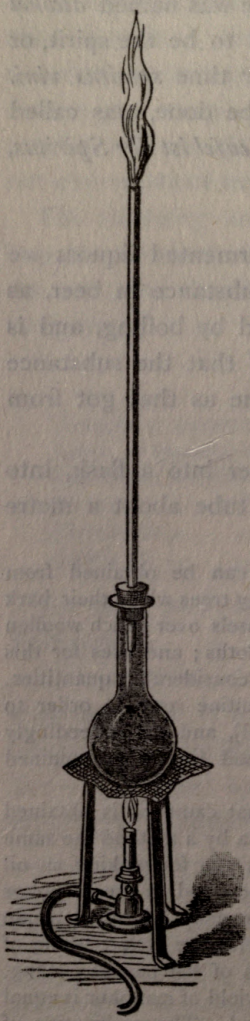


Fig. 17.

A great deal of spirit is distilled at the present time from wine; this spirit once sufficed for the total requirements of the world, but to-day it is used for making brandy. Beer, however, has never been used as a source of spirit, because a method of obtaining spirit from grains was discovered long ago, and this method is much less complicated than the brewing of beer.

The process seems to have been invented in South Germany about the year 1500. The main points in the manufacture are as follow.

The raw material is rye, or a mixture of barley and rye. [Maize, rice, oats, sugar, and molasses are also made use of in this country; but barley is the substance generally employed.] The earlier stages in the manufacture are similar to the earlier stages of brewing; moistened barley is allowed to germinate; but the malt

thus formed is not generally dried—as is done in beer brewing—but is subjected to further treatment.

The diastase of the malt, which brings about the change of starch into sugar and dextrin, is able to effect this change in a much larger quantity of starch than that which is contained in the malt. If the mashed rye [or barley], which has been boiled with water in order to set free the starch granules, is covered with water at about 60° C. [140° F.], and malt is then added, all the starch in the grain as well as that in the malt can be converted into sugar. The sweet liquid thus produced is then subjected to fermentation by means of yeast which the distiller prepares for his own use.

The preparation of yeast is closely associated with the production of what is now generally called pressed or dry yeast (*Presshefe*) [German yeast], which is so convenient that it is almost always employed nowadays for bringing about fermentations. This yeast is used by the bakers of wheaten bread (see p. 86); and also when bread is baked at home. The procedure used to be as follows. The fermentation whereby the yeast for use in making spirits was to be produced was carried on energetically, and was of the kind called high fermentation [that is, the yeast is carried to the top of the fermenting liquid by the stream of carbonic acid which is freely produced]. For this purpose a wort was prepared from one part malted barley and five parts crushed rye ; yeast was added, and the temperature was kept up to nearly 40° C. [104° F.], which is much higher than that whereat fermentation is usually conducted. After 1895, it became customary to lead air into the fermenting wort, as that was found to promote growth of yeast and to increase the yield. The fermentation was conducted at a high temperature because that was required to produce lactic acid in quantity sufficient

to keep the fermentation going. Since 1900, the process has been conducted by adding a little sulphuric acid, in place of depending on lactic acid produced in the operation. This modification greatly quickens the process, and increases the yield of yeast. The astonishing advance made in this part of the fermentation industry is shown by the following data. About 14 to 15 per cent. yeast, and about 30 to 32 per cent. spirits, was obtained from 100 parts of grain; after a time the percentage of yeast was increased to about 20 per cent., and that of spirits decreased to about 20 per cent. Since the use of sulphuric acid became common, about 40 per cent. yeast is obtained, with only about 12 per cent. spirits.

In order to prepare dry yeast, a workman skims off the masses of yeast from the surface of the liquid, and places them in a hair sieve floating on water in a barrel. The yeast cells pass through the sieve and gradually settle down to the bottom of the barrel, while all the coarser particles of solid matter remain in the sieve. When the yeast has settled the water in the barrel is drawn off, fresh water is added and is shaken up with the yeast, which is then allowed to settle again, and these processes are repeated several times. When the last lot of water has been drawn off the yeast is left as a fine mud-like deposit, which is dried by pressure.

The sweet liquid prepared in the way already described from malt and mashed rye [or barley] is caused to ferment quickly, for the purpose of making spirits, by adding active yeast to it. The special method used in the fermentation is closely connected with the way in which the excise duties on spirits are levied. And the method which is most in harmony with the excise arrangements, which arrangements differ very much in different countries, is found to pay the best. The fermented liquid is finally distilled, and the distillate, which, like the spirit from wine, has an agreeable odour and flavour,

is used for making various kinds of liquors. [Whisky is made by re-distilling, and so concentrating, this distillate; it contains from 60 to 78 per cent. alcohol by weight.] The residue left in the distilling vessels is known as *vinasse*; we shall speak of this immediately.

Spirits have been obtained from potatoes since about the year 1820. Although there is nothing of a spirituous nature in potatoes, yet when we remember what large quantities of starch they contain we at once see that an alcoholic liquid can be obtained from them by first converting their starch into sugar.

Indeed, a glance at the numbers which represent the average compositions of growing potatoes and rye shows that much more spirit can be obtained from a given piece of land by raising potatoes than by growing rye thereon. About 1,600 kilograms of rye are harvested, on an average, from a hectare of land; and as rye contains about 65 per cent. of starch this is equivalent to about 1,040 kilograms of starch. But about 16,000 kilograms of potatoes are obtained, on an average, from a hectare of land; and, taking the starch in potatoes as not more than 18 per cent. on an average, this corresponds to 2,880 kilograms of starch. [One acre yields $12\frac{1}{2}$ cwts. rye, equal to $8\frac{1}{5}$ cwts. starch; and one acre yields 125 cwts. potatoes, equal to $22\frac{2}{5}$ cwts. starch.]

When the process of manufacturing spirits from potatoes had once taken root it flourished exceedingly, especially in the Eastern Elbe provinces of Germany; and these provinces were much enriched for many years by this industry.

We know that the starch granules of potatoes are enclosed in a husk (see p. 84). The custom in the manufacture of spirits was to set the granules free from the husks by boiling; but the experience of years has shown that all the granules

cannot be so thoroughly deprived of their husks by this simple plan as to enable the diastase to convert them completely into sugar. That this transformation into sugar may be completed, which must be done if the maximum yield of spirit is to be obtained, it is now customary to boil the potatoes in closed vessels, and not, as formerly was done, in open vessels.

It is more difficult to cause water to boil in a closed than in an open vessel. Just as water boils much under 100° C. [212° F.] in a vessel from which the air has been removed (see p. 75), so the boiling-point is raised above 212° F. in a closed vessel, because of the pressure on the surface of the water of the water-vapour which cannot escape from the vessel. When the pressure on water is increased to four times that of the ordinary pressure, or, as is generally said, to four atmospheres, the water does not boil until it attains the temperature of about 150° C. [302° F.]; and the custom is to heat water with the potatoes under this pressure, and therefore to this temperature, in vessels called steamers. When the water in the steamers is boiled it of course attains the temperature of 150° C. [302° F.]; when this temperature is reached a valve in the bottom of the vessel is opened suddenly, and the contents are forced out into barrels placed ready to receive them. The excess of pressure is at once removed, and the water, some of which is enclosed in the cells of the potatoes, and which is too hot by 90° F., suddenly becomes vapour, for the formation of which the whole of the excess of heat must be employed. The result is that all the cells are thoroughly broken up, and the starch granules are set free so completely that they can all be acted on by the diastase and converted into sugar.

The next process consists in adding barley malt to the potatoes, mashed with water, and so converting the starch

into sugar. This sweet liquid is then fermented by yeast in the way we have already described. Finally the liquid is distilled, and the spirit is thus obtained.

The residue from the preparation of potato spirit, as well as that from the manufacture of spirit from grain, is known as *vinasse*. This substance is an excellent food for cattle; for a little consideration will show that, as only the starch is removed from the grain or the potatoes, the nitrogenous substances—that is, the albuminoids—remain as such in the residue. Now we know that these substances are exceedingly nourishing; hence the distilling of spirits makes it possible for the agriculturist to maintain a greater head of cattle than he could support on the same quantity of land without the aid of this manufacture, and in this way spirit-making furthers agriculture.

The spirit obtained in the potato distilleries is, however, very different from that produced from wine or grain. The latter spirit can be used directly for making whisky, brandy, etc., as it has an agreeable flavour and odour. But the raw potato spirit must be purified in spirit refineries before it can be used as a liquor. For when potato wort is fermented there is produced, besides ordinary alcohol and carbonic acid, a series of other compounds, which, although they are classed by chemists among the alcohols, nevertheless act on the human organism in a way very different from that of ordinary alcohol. These substances are chiefly *amyl alcohols*, to give them their chemical name, and these alcohols, which are all classed together in ordinary language under the name of *fusel oil*, act as poisons; the smell of them is oppressive and causes choking. They must therefore be removed from the raw spirit; this removal is effected on the large scale in the following way.

The raw potato spirit usually contains about 80 per cent. alcohol and 20 per cent. water, together with fusel oil dissolved in these. If water is added until there is about 50 per cent. of alcohol in the liquid, the fusel oil, being no longer easily soluble in this diluted spirit, separates in very fine drops which cause the liquid to become turbid. The liquid diluted to 50 per cent. of alcohol is filtered through wood charcoal; the fine drops of fusel oil adhere to the charcoal, and are thus removed from the liquid. At the same time the charcoal removes the colouring matter and the substances which impart an objectionable odour to the alcoholic liquid (cf. p. 42).

The filtered alcoholic liquid is now brought to a percentage of 96 per cent. alcohol, by a method based on the following principle.

We remember that we found it possible to burn out the alcohol from beer, after a long glass tube had been attached to the flask wherein the beer was boiling. No explanation was given at the time of the reason for using so long a tube, because to stop then and explain would have taken attention away from the main point of the experiment; the tube was made long in order that the alcohol vapour might be completely separated from the water vapour. Had we attempted to set fire to the alcohol vapour at the mouth of the flask we should have failed, because the vapour of alcohol was mixed with so much water vapour at that point that the mixed vapour would not have ignited. But a separation of the vapours was effected by causing them to pass through the long tube, inasmuch as the heavier water vapour fell behind the comparatively light vapour of alcohol, and the latter issued from the upper opening of the tube mixed with so little water vapour that the alcohol took fire when a light was brought to the end of the tube. Spirit is made as con-

centrated as possible, by the use of this principle, in order to save cost of carriage ; this is done by fitting to the distillation vessel a long cylindrical apparatus adapted internally for the purpose of separating the vapours of alcohol and water. Spirit obtained in this way never contains more than 96 per cent. of alcohol, as the remaining 4 per cent. of water is chemically combined with the alcohol.

It is only within the last hundred years that alcohol of 100 per cent., that is, quite free from water, has been prepared. This is done by adding burnt lime to the 96 per cent. spirit ; the burnt lime is slaked by the water in the spirit, that is, the water enters into chemical union with the lime, so that when distillation is again carried out the water is retained by the lime, and *absolute alcohol*, that is, alcohol of 100 per cent., passes over.

Since 1904 the preparation of spirits from wood has become an important industry. When wood is boiled with sulphurous acid, a liquid is obtained which can be fermented by yeast. The manufacture of spirits by this process was greatly developed in America ; as much as 8 litres of spirits have been obtained from 100 kilograms of wood shavings [nearly 2 gallons from 2 cwts.]. But this method has been overshadowed by the discovery, made in 1908, that spirits can be prepared from the residue obtained in making cellulose from wood, that is, from material which costs nothing. We know that sugar is prepared from raw sugar, but that sugar already exists in certain plants. The sap of the maple tree is rich in sugar. About 9,000,000 kilograms [about 9,000 tons] of maple sugar are made yearly in Canada. This sugar has an agreeably aromatic, somewhat bitter taste. It is not then to be wondered at that sugar should be found in fir and pine trees. When the wood of fir or pine trees is boiled with acid sulphite of lime for the preparation of

cellulose—we shall learn more of this process in Lecture VIII.—sugar goes into solution in the liquor. When this liquor is treated with yeast, under proper conditions, the sugar in it ferments; 100 kilograms of wood yield about 3 litres spirits [about $\frac{3}{4}$ gallon of spirit from 2 cwts. of wood]. Strange to say, this spirit is *denaturalised* (see forward), inasmuch as a substance (called *wood-spirit*) is present in the liquor which distils over with the spirit, and renders it undrinkable.

This is the place to mention *methylated* or *denaturalised spirit*. As alcohol and alcoholic drinks are used as beverages they are favourite subjects for taxation in all countries. But the manufacture of spirits is advantageous to the farmer, not only by giving him spirit itself, but also by providing him with a valuable fodder for cattle in the form of the residues from the processes of distillation. It cannot be to the interest of the State to place hindrances in the way of a manufacture which is so advantageous to the farmer, provided the State can arrange the tax so that it shall fall upon the spirit consumed as a beverage, and place an obstacle in the way of excessive drinking. Why, for instance, should the State tax spirit to be used for heating purposes? It does not tax wood or coal.

Some means must be found for insuring that spirit meant for heating purposes, or for use in various industries, cannot be consumed secretly as a drink. Spirit must be robbed of those properties for which people drink it; its nature must be changed.

This purpose is effected by adding substances which do not alter the combustibility, etc., of the spirit, but by their odour and taste make the spirit undrinkable, and cannot be removed except by those who have considerable

chemical knowledge and have also suitable apparatus at their command. *

[*Methyl alcohol*, or, as it is more commonly called, *wood naphtha*, is the substance used in Great Britain for this purpose. In 1855 the Board of Inland Revenue sanctioned the employment in various industries of a mixture of nine parts ethylic alcohol (spirits of wine) and one part methylic alcohol, and they agreed to allow the use of this *methylated spirit* duty-free under certain restrictions.]

The preparation of pure spirit for making spirituous liquors is not to-day a very difficult undertaking. The shops where these liquors are sold are generally still called distilleries [in Germany]. This name is a survival from the time when the proprietors of the shops themselves carried on the preparation of distilled liquors on a small scale, whereas nowadays the industry is conducted by large manufacturers.

Liqueurs are now made, very conveniently, by diluting the spirit obtained from the large manufacturers till it acquires the proper taste, and then adding sugar, and one or more of those fruit essences which are extracted from various fruits

*The substances allowed by the law to be used for this purpose [in Germany] are what are called *pyridine bases*. We have already learnt that tar is produced in gas making, besides ammonia, which is a compound of nitrogen and hydrogen. The tar contains certain nitrogenous substances which can be defined chemically as derivatives of ammonia, and which, like ammonia, have a very marked odour; some of them indeed have an exceedingly disagreeable odour. Among the products of the distillation of gas-tar, a process we shall have to consider hereafter, are those pyridine bases that are used for mixing with spirit for the purpose already indicated. As their name implies, these substances are capable of uniting with acids to form salts (see p. 49).

[I have put this part of the text in a footnote, and have replaced it by the sentences in a square bracket, because of the differences between the German and the English methods for making spirit undrinkable.—TR.]

and are sent into the market by the manufacturer. It is possible to prepare such *fruit ethers* by purely chemical methods, without using fruits at all; and those that are prepared in this way are more and more driving out of the market the essences obtained from the fruits themselves.

Many *liqueurs* are made by soaking the flowers of plants, for it is chiefly these that are used, for a long time in spirit, and then drawing off the liquor which has acquired the odour of the flowers and also a peculiar flavour.

Brandy, arrac, and rum are not, however, prepared in this way. They are made by the direct distillation of fermented liquids; and each owes its peculiar flavour to certain substances which volatilise and condense in the process of distillation.* Brandy is distilled from wine; the colour is derived from the vessels of oak wood wherein it is stored. Arrac is made in India, chiefly by distilling fermented rice. The preparation of a spirituous liquor from rice is similar to the process we are accustomed to use in preparing corn spirit. Rum is manufactured in the West Indies from fermented sugar molasses (see p. 76).

As these three liquors are free from sugar, as must be the case from the methods of their preparation, they may be used without harm by patients suffering from diabetes, by whom *liqueurs* must be avoided.

The following analyses show the quantities of the most important ingredients in some of the spirituous liquors commonly consumed:

	Alcohol.	Sugar.
Brandy	53·82 per cent. by volume	—
Arrac	60·74 „ „	—
Rum	77·62 „ „	—
Kümmel	33·90 „ „	31·18 per cent.
Benedictine ...	46·20 „ „	32·57 „ „

* These substances may be called raw spirit with a very agreeable flavour.

Before leaving this part of our subject let us examine the question, which we have hitherto passed over, as to how far alcohol can be said to possess any value as a food. In what has been said hitherto we have followed the example of all the standard authors in regarding this value as non-existent. At the same time we must say that, if starch and sugar are foods because the carbon which they contain is finally burnt in the body to carbonic acid, then alcohol, which is a substance intermediate between sugar (or starch) and the final product of the decomposition of sugar—namely, carbonic acid—will also be wholly burnt, in the long run, in the body. Indeed, as the composition of alcohol is simpler than that of the fats in the body, which fats are eventually burnt in the organism, alcohol ought to be more easily oxidised than these fats, and therefore the use of alcohol should lead to some saving in the consumption of these substances. Nevertheless many experiments have shown that the significance of alcohol as a source of nourishment for people in good health is extremely small.

On the other hand, experience shows that matters may be very different in cases of illness. It is apparent to every one that the loss of energy from which sick people suffer, who cannot consume the ordinary kinds of food, may often be relieved by the use of wine or champagne which they will take with pleasure. This can only be explained by supposing that, although fats and albuminoids are burnt with difficulty in the bodies of those who are weakened by illness, nevertheless alcohol, which is more easily oxidised than these two substances, can be oxidised even in their weak condition without too much difficulty, and can in this way supply the heat and the vital energy which are required.*

* I have omitted a few paragraphs wherein the author sets forth his opinion regarding the use of alcohol and its effects on the human organism.—TR.

LECTURE VI

Wine vinegar—Wood vinegar—Glacial acetic acid—Wood spirit—Acetone—Gunpowder—Greek fire—Fulminating mercury—Gun-cotton—Dynamite—Collodion—Blasting gelatin—Cordite—Chlorate explosives—Wool—Cotton—Silk—Artificial wool [Shoddy]—Carbonising—Mercerised cotton—Artificial silk.

WE begin to-day with vinegar.

Experience shows that wine and beer, which are alcoholic liquids, become sour when they are exposed to the air for some time. These liquids lose their intoxicating properties, and become so sour that they are undrinkable except when mixed with other substances. The new liquids, however, are used as adjuncts to food, to which they impart an agreeably sharp flavour.

When an alcoholic liquid becomes sour the alcohol in it is changed to acetic acid, and the liquid thus produced is called *vinegar*.

We have learnt that the juice of grapes very easily changes into wine. The transformation of wine into what is called wine vinegar takes place almost as easily, and for this reason wine vinegar has been known since very early times.

The production of acetic acid from alcohol consists in an oxidation of the latter substance; this addition of oxygen, and therefore the passage from alcohol to acetic acid, is easily carried out in the laboratory. But the change is effected by

atmospheric oxygen only in the presence of a certain mould, to which the name *Mycoderma aceti* is given. This mould is found everywhere in the air; it is active in liquids which already contain vinegar.

The preparation of wine vinegar is carried on nowadays in the following manner. Boiling vinegar is poured into oaken barrels so as to soak the wood thoroughly, and the barrels are then filled to about two-thirds with wine. A series of holes is made in the barrels above the level of the liquid in order that air may have free access to the surface of the liquid. The change is complete after about fourteen days. Half of the liquid is drawn off to be sold as vinegar, and the barrels are filled up with fresh quantities of wine. The process may go on for some years before it is necessary to clean the barrels.

It is necessary for the normal process of acidification that the wine should not contain more than about 10 per cent. of alcohol. Stronger wines must be diluted with water.

Cider, perry, and beer can be manipulated in a similar way. Vinegar made in this way from ordinary beer retains a bitter aftertaste, derived from the hops, which cannot be removed. For this reason it was once customary to prepare a beer without hops, for the special purpose of manufacturlng vinegar from it.

As the process of making vinegar consists essentially in the oxidation of alcohol any kind of commercial spirit may be employed for the purpose; and large quantities of vinegar are made to-day from commercial spirits. The spirit must be diluted until it contains not more than 10 per cent. of alcohol; it is then treated in the way already described for making vinegar from wine. The yield of vinegar is, however, much smaller when spirit is used than when wine is employed; for the souring of spirit is as difficult as the souring

of wine is easy. For this reason another method has been employed since about 1820 for making vinegar from spirits; this is called the *quick vinegar process.*

A deep wooden vat, provided with a false bottom, is filled up with shavings of beech wood, which experience has shown to be the most suitable wood for the purpose. The shavings are thoroughly soaked in vinegar, and dilute spirit is allowed to trickle slowly on to the shavings from the top of the vat. Many holes are bored in the sides of the vat in such a way that air can enter, but liquid cannot escape, through them. The alcoholic liquid is thus spread over a very large surface while it is exposed to the oxidising action of the air. The acidified liquid collects beneath the false bottom ; it is drawn off, and passed through the same vat three or four times before the oxidation is completed.

The strongest vinegar that can be obtained by this method contains about 10 per cent. of acetic acid. The following analytical results show the quantities of acetic acid in various vinegars:

Strongest vinegar	10·30	per cent.	acetic acid.
Wine vinegar	5·37	„	„
Ordinary white vinegar	4·63	„	„
Ordinary brown vinegar	3·53	„	„

Brown vinegar may derive its colour from being prepared from beer brewed without hops or from red wine ; but it is more often coloured by a little burnt sugar (see p. 71).

Vinegar essence can be bought to-day containing from 25 to 50 per cent. acetic acid, from which ordinary household vinegar is made by adding water.

The essence cannot of course be made by the method already described, inasmuch as that method is not applicable to liquids which contain more than 10 per cent. of

alcohol, and therefore produce a corresponding percentage of acetic acid.

The source of this vinegar essence is quite different from that of ordinary vinegar; it is made by the dry distillation of wood. We have already dealt in detail with the dry distillation of coal (see gas making, p. 28), the chief products of which are gas, an aqueous liquid (ammonia water), tar and coke. Products corresponding with these are obtained by the dry distillation of wood. But gas from wood cannot compete with coal-gas, and is scarcely used, while the watery liquid obtained by the distillation of wood is not basic, like ammonia water, but has acid properties. This liquid contains acetic acid, mixed with a great many other substances which are used in ordinary life, just as the crude acetic acid is used under the name of wood vinegar. The residue in the retorts is wood charcoal.

Wood spirit is one of the liquid products of the dry distillation of wood. The chemical composition of this substance is that of the simplest possible alcohol. Like fusel oil, it is undrinkable; it is much used in England for adding to ordinary alcohol to produce methylated spirit (see p. 113). Another product of the dry distillation of wood is a clear, colourless liquid called *acetone*, the chemical composition of which is not so simple as that of wood spirit. This substance is made use of in the production of aniline colours; it is also much used as a solvent, and in this *rôle* we shall meet with it again when we are considering the preparation of smokeless powder. As but little acetone is found in the products of distilling woods, this compound is prepared in other ways also.

But it is the acetic acid in the liquid obtained by distilling wood which interests us most at present. The acetic acid in

this liquid is coloured brown by the presence of tarry matters. Pure acetic acid, free from water, is obtained from this brown liquid by a somewhat complicated process of purification. Pure acetic acid is a clear, colourless liquid, with a very strong odour of vinegar; it has the property of solidifying at a low temperature to a solid very much resembling ice, which solid becomes liquid again at 17° C. [62·6° F.]. Because of this behaviour pure acetic acid is commonly spoken of as *glacial acetic acid*, a name which is quite superfluous and has a flavour of mystery about it. When the acid is diluted with its own weight of water it is known as vinegar essence.

We have now said enough about the relations of foods and condiments to human life; and we shall proceed to consider other subjects which require some chemical knowledge for their elucidation.

We have already made mention of saltpetre in speaking of the use of soda saltpetre as a source of nitrogen to the agriculturist (see p. 50). Potash saltpetre, however, is used for a very different purpose; it is the foundation of all the varieties of gunpowder, a substance which is now being partially supplanted by the smokeless powders introduced about the year 1886.

Potash saltpetre is the salt that is formed by combining the base potash with nitric acid (see p. 49). Now if nitric acid is allowed to react with such an organic substance as *cellulose* (regarding which we shall learn more when we consider the manufacture of paper), a compound is formed by the nitrogroup of the nitric acid entering into the molecule of the cellulose; this nitrogroup consists of an atom of nitrogen combined with two atoms of oxygen. The compound formed in this way is called *nitrocellulose*; this

compound, and others similar to it, form the basis of the newer explosives and also of smokeless powder, substances which have to be dealt with later.

The compound of nitrogen and oxygen which is fixed in gunpowder in the form of saltpetre is also, in the form of the nitrogroup, the explosive ingredient in all modern smokeless powders. Notwithstanding innumerable attempts, no better or equally good substitute for this compound has been discovered.

Neither the Greeks nor the Romans were acquainted with saltpetre, nor with any mixture resembling gunpowder. Saltpetre seems to have come into Europe in the fifth century, from India or China, by way of Constantinople.

The discovery was made in the Arsenal at Constantinople that if combustible substances were mixed with saltpetre these substances could be burned in such a way that the burning did not cease until the mixture was entirely consumed. We now know that this property of saltpetre is connected with the large quantity of oxygen, 47·5 per cent., which the salt contains. The saltpetre brings oxygen, which we know to be the most important element in processes of combustion, in the solid form, into any mixture of which the saltpetre is an ingredient.

It was soon found that the most suitable mixture for burning was one made of saltpetre, charcoal, and sulphur. The mixture was known as *Greek fire*, and by its use Constantinople was able to defend herself for a long time from all her enemies. The Arabian fleet was burnt by the use of this substance in the seventh century, and at last the Arabs abandoned the attempt to conquer the city. Western Europe, which did not possess this means of defence, could not resist the Arabs, who crossed into Spain in 711, and for many centuries ruled that country. In the tenth century

Constantinople used Greek fire to drive back an inroad made by Bulgarians. This substance, Greek fire, has evidently played an important part in the development of the nations, and the discovery of the modification of Greek fire which we call gunpowder has increased this influence. It is a noteworthy fact that, although all these peoples who fought against Constantinople tried to discover the secret of making Greek fire, nevertheless the secret was kept for five or six hundred years. Such a fact seems to us to be almost inexplicable. We cannot understand how a discovery of so much importance should have been made so long ago, nor how the city that was in possession of this secret should have been able to keep it almost up to modern times.

The earliest writings that give an account of the composition of Greek fire are those of the Byzantine author Marcus Græcus, who lived about the year 1200. A Latin translation of a book by this author has come down to us; its title is *Liber Ignium ad Comburendos Hostes (Book of Fires for destroying the Enemies)*. It does not appear from this book that Marcus Græcus was the first to publish to the world the secret of making Greek fire; it rather seems as if the knowledge of the manufacture had already spread by word of mouth, and that Constantinople could no longer claim the monopoly of the process.

The book of Marcus Græcus always speaks of Greek fire as merely a very combustible mixture, although the composition of the mixture described in the book is not very different from the compositions of the gunpowders that are used to-day for military purposes. The following figures show this:

	Greek fire, according to Marcus Græcus.	Prussian military gunpowder in 1886.
Sulphur	11 per cent.	10 per cent.
Carbon	22 „	16 „
Saltpetre	67 „	74 „

There is now no chance of finding out when and by what means the discovery was made that a most energetic explosive power was hidden in this mixture—an explosive power which was indeed greater than that of any other artificially produced substance then known. This discovery was soon turned to account for the purposes of war ; the first metal cannons were cast at Florence in 1326, and soon after this we find enumerations of the pieces of artillery brought into action in the battles and sieges of the period. But the explosive was not used in hand weapons until a much later period. About the year 1500 soldiers who used guns stood in files thirty-seven deep ; the reloading of the weapons occupied so much time that when a man had fired he passed to the rear, and he was not ready to fire again until the thirty-six men in front of him had discharged their weapons. This state of affairs lasted till the time of Frederick the Great, when such great improvements were made in flintlock guns that, since then, the gain or loss of battles has depended very largely on the fire of the infantry.

The use of gunpowder as an explosive agent in mining did not begin until 1627.

Many attempts to improve gunpowder have of course been made from time to time ; but the figures already given show that the changes made in its composition have not been very marked. In former times the preparation of gunpowder was a very simple operation ; the three ingredients were mixed and the thing was done. In the nineteenth century, great advances were made in this, the purely technical part of the manufacture. The method of mixing the powder which is made in the largest quantities, that, namely, for use in mines, had been carried to very great perfection, and at the same time the most suitable size of grains had been found out

long ago. Powder to be used in large cannons, for instance, was pressed into the form of six-sided prism-shaped pieces, several centimetres long. The pieces of this prismatic powder were pierced with holes, which insured the simultaneous burning of the grains from within and from without. Nevertheless, this powder burnt much more slowly than that made in fine grains. Hence the force of the explosion in a tube took effect more slowly when large grained powder was used, and for this reason powder of this kind was more effective in the modern very large cannons.

We have mentioned only one of the advances, based on logical reasoning, that have been made in the preparation of the most useful kind of powder, to make clear that, although gunpowder reminds us of Greek fire so far as its composition is concerned, yet the Greek fire, that was thrown like a burning torch at the enemy, was merely a plaything compared with the modern powder.

The following figures show what can be done with prismatic gunpowder. A cannon exhibited by Krupp at the Chicago exhibition, when charged with 115 kilos. [253 lbs.] of this powder propelled a shot weighing 215 kilos. [473 lbs.] to a distance of 20,226 metres [12½ miles]; the flight of the shot occupied 71 seconds, and the highest point attained was 6,540 metres [4 miles] above the earth, while the height of Chimborazo is only 6,421 metres [3·99 miles].

The great advances recently made in chemistry have led to a complete revolution in regard to gunpowder. Very explosive substances have long been known in the laboratory, but the extraordinary violence of their action made it impossible to use them in guns, because they would burst the gun before they could set the shot in action. Only one compound found an application in connection

with guns, and that was *fulminating mercury*, a substance which explodes when struck sharply. It was used in percussion caps for starting the explosion of the powder in the gun, in place of the flintlock which had succeeded the untrustworthy and unsafe tinder. In the flintlock the igniting spark was produced by the fall of a piece of steel on flint.

When gunpowder explodes a great deal of smoke is produced. The smoke consists of compounds of the potassium contained in the nitre of the powder. This very stable metallic substance is changed during the explosion into sulphate of potash and other similar compounds; these substances are solids, and they are broken up by the explosion into a very fine dust that floats in the air for a long time and forms the smoke of the powder. Matters are quite different when a little guncotton is ignited—and we must now proceed to consider this substance; the guncotton burns instantaneously and without a trace of smoke.

Why then should there be this great difference between the old and the new explosive substance? Cotton wool consists of *cellulose*, a compound of six atoms of carbon, ten atoms of hydrogen, and five atoms of oxygen; it has therefore the same composition as starch (see p. 67); it is a carbohydrate. When cotton wool is treated with nitric acid, the action of which is increased by the addition of sulphuric acid—the mixture of these acids is technically known as "*nitroacid*"—nitrogroups enter into the cellulose molecule, as has been mentioned already. While the old powder was a mixture of substances prepared as carefully as possible, the new explosive substance is itself a chemical compound. The old powder burnt away; when the new

substance is used as an explosive there ensues an instantaneous falling to pieces of the molecule. While a kilogram ($2\frac{1}{5}$ lbs.) of powder requires about the hundredth part of a second for its combustion, about one-fifty-thousandth part of a second suffices for the decomposition of a kilogram of guncotton.

When guncotton is burnt carbonic acid is produced from the carbon and water from the hydrogen, and the necessary oxygen comes partly from the cotton wool, but more particularly from the nitrogroups—for several nitrogroups enter into the molecule of cellulose when guncotton is made. The nitrogen of the nitrogroups is given off as nitrogen. As we have seen, the explosion of this material produces gaseous substances only, for the water that is formed is gaseous at the high temperature whereat the burning is completed. As these gases are colourless they are of course invisible; guncotton therefore burns without any smoke.

Guncotton was the first of the more recently discovered explosives that was found to be practically useful; and soon after its discovery, which was made in the year 1846, many countries laid in great stocks of this substance. But the stores of guncotton sometimes exploded suddenly without any apparent reason, and caused enormous damage. All confidence in the material was lost; but after about thirty years' labour such definite knowledge has been obtained regarding the conditions of preparation of a stable substance that guncotton can now be handled without danger. It was also discovered after a long time—and this fact has proved very important—that wet guncotton is as convenient as the dry material, or even more convenient, for explosive purposes. And nowadays torpedoes charged with rolls of moist guncotton which has been subjected to enormous pressures are possessed of such great destroying power that

even the best defended vessels cannot withstand the impact of these weapons.

The charging of these torpedoes is perfectly safe, inasmuch as moist guncotton obstinately refuses to ignite when brought into contact with an ordinary flame. Explosion takes place only after burning has been started; and this fact is the essential part of the most important discovery just mentioned.

To say that explosion occurs only after burning has been started means that the guncotton must receive a shock which in the physical sense is extremely sharp. Such a shock is produced by the explosion of fulminating mercury, for instance. If a detonator of this material is exploded in a mass of moist guncotton the explosive wave causes a disruption of the atoms which are arranged in a definite way in the molecule of the guncotton—or *nitrocellulose*, as this substance is called in chemistry—resulting in the falling to pieces of the molecule, and hence in the explosion of the guncotton whether that be wet or dry.

Long before it had become possible to handle guncotton with perfect safety, another of the modern explosives had come into favour for the peaceful purposes of mining, etc.; this was *dynamite*, a substance the name of which is now heard everywhere in the world.

We have already got to know something of glycerin as a constituent of fat (p. 19). When glycerin is mixed with "nitroacid" (see p. 25) three nitrogroups are taken up by the glycerin; the product is therefore very rich in this most powerful constituent. The *nitroglycerin* produced in this way is a liquid, like the material from which it is made, and it is not very suitable for use as an explosive. It is therefore mixed with a sufficient quantity of very fine sand, called *infusorial earth* (*Kieselguhr*), to produce a solid mass, and

this solid is known as dynamite, a substance that was employed in blasting the St. Gotthard Tunnel, and in many other works of a like character.

Meanwhile quantitative deductions from the theory of projectiles had shown that much more efficient results would be obtained by decreasing the diameter of the projectiles to be used in cannons, provided that a greater impulse than was possible by the employment of gunpowder could be given to the shots. Thereupon began the search after new kinds of military powders—which should necessarily be smokeless, for reasons we can now understand—on the lines suggested by the properties of the nitrocompounds. The discovery by the French of *melinite* was one of the results of this search. Melinite was prepared by the action of "nitroacid" on *carbolic acid*, a substance much used as a disinfectant. The result of this action is to introduce three nitrogroups into the carbolic acid, and so to form *picric acid*, which is a compound that, like guncotton, can be exploded when moist by an initial detonation. The methods of preparation of this powder are kept as a State secret; but the substance has not stood the test of time. Guncotton seems to have come out victorious in all contests with this competitor, as with the other competitors in the domain of modern smokeless powders. At any rate guncotton appears to be a constituent of all these powders, as far as one can find out considering that the methods of manufacture of smokeless powders are kept secret by the different states.

What makes guncotton so very suitable is its property of dissolving in various solvents and so producing a liquid that is eminently adapted for making powders. For instance, the well-known substance *collodion* is a solution of guncotton in a mixture of ether and alcohol. If this solution is

evaporated a film remains, which can be obtained of any desired thickness; by cutting this film into small pieces a smokeless powder is produced. The technical preparation is not so easy as this, but still it is carried out on these lines.

As guncotton alone would be too violently explosive for use in guns it is customary to add some indifferent substance —camphor, for instance, was used for a long time—to a solution of guncotton; and then to evaporate the solution; in this way a solid is obtained, which may be regarded as diluted guncotton, and can be used as a smokeless powder. It is evident that a powder of any desired strength, and suitable for various purposes, can be obtained by this method of procedure.

The most powerful of all explosives is made by saturating guncotton with nitroglycerin; this explosive is used in mining operations, but it cannot be employed in guns. Guncotton does not dissolve in nitroglycerin, but it swells up and forms a jelly-like substance which is known as *blasting gelatin.* This blasting gelatin is the most energetic explosive we have at our disposal: the strength of it can be modified by using more or less guncotton; and it seems, from what has been said already, that this explosive cannot be surpassed, for the energy of nitroglycerin is not lessened in it by the addition of such a substance as sand, as is the case in making dynamite, but is rather increased by the guncotton that is employed in the manufacture.

If the nitroglycerin is diluted with acetone (see p. 119) before the guncotton is added, and indifferent substances are then added for the purpose of diminishing the explosive force of the powder that is to be prepared, and if the greater part of the acetone is then removed by evaporation, the substance that remains can be made into long threads of any

desired thickness by the help of machines. *Cordite* is prepared by evaporating the rest of the acetone from these threads; this smokeless powder (the name of which is derived from the word *cord*) is used in the English army. The explosive force of cordite can be modified by adding greater or smaller quantities of indifferent substances to the solution from which it is obtained.

Many attempts have naturally been made to prepare suitable powders or explosives by methods quite different from those that have been described. If, for example, the nitrogen atom in saltpetre is replaced by an atom of chlorine, the new compound *chlorate of potash* is obtained. Thus

KNO_3	$KClO_3$
Nitrate of potash.	Chlorate of potash.

The abbreviation for nitrogen is N, the first letter of the name; the abbreviation Cl is used for chlorine, that is the first and third letters of the name. The formulæ which are written with the help of these contractions show very clearly the chemical similarities of the two compounds we are speaking of.

Chlorate of potash was discovered by Berthollet towards the end of the eighteenth century. He proposed that it should be used as a substitute for saltpetre. The French Government attempted to make gunpowder containing this compound. The manufacture began one morning; by the afternoon several workmen, and a lady who happened to be in the factory, were dead. The extraordinary sensibility to friction, or shock, of mixtures containing chlorate of potash made it impossible, for at least a hundred years, to prepare explosives by the help of this substance. Nevertheless, extremely active explosives containing chlorate of potash have been prepared in Germany since 1908. Oil or wax is added to the mixture; these substances diminish the friction. The product explodes only after an initial

burning has been started. The manufacture can be conducted without danger.

Superficially mixed preparations of chlorate of potash and similar compounds with other substances are employed in making fireworks; these mixtures are poured into covers, generally of a cylindrical shape, in which they are gradually burned.

We must not omit the mention of some of the applications of nitrocellulose to peaceful purposes. The manufacture of artificial silk from nitrocellulose will be described on p. 134. In 1877 Hyatt discovered that a mixture of guncotton and camphor is changed, by heat, into a uniform, horn-like substance, which can be shaped into any desired form, and has many and very useful properties. This substance, under the name *celluloid*, has found very diverse applications. The great drawback to the use of celluloid is its remarkable inflammability. Nitrocellulose is made by treating cotton-wool with nitric acid; after innumerable experiments it was found, in 1907, that by using acetic acid in place of nitric acid a substance is obtained which so far resembles nitrocellulose that it may be used to prepare a sort of celluloid. This substance is known as *cellite*; unlike celluloid, it is difficult to set fire to.

The pieces which drop off in making celluloid articles are used for manufacturing *artificial leather*. They are dissolved in spirit, oil is added, and cotton-cloth is steeped in the liquid. When the spirit is evaporated a substance is obtained which has the feel, flexibility, elasticity, and impermeability by water, of leather. By passing the artificial leather through hot rollers the grain of leather is so well imitated that even an expert cannot distinguish it from genuine leather merely by looking at it. The discovery of this method of making artificial leather was made by Gevaert. Because

of the constant rise in the price of leather the demand for this excellent substitute increases. It serves well for making the uppers of cheap shoes.

We must now speak of the substances used for clothing. Substances made from both animal and vegetable fibres are used for this purpose, and leather is also employed.

Fibres of animal origin are very different chemically from the fibres of vegetable substances, inasmuch as the former contain nitrogen, but the latter do not contain this element. If animal fibres catch fire they produce badly smelling nitrogenous substances—they are said to smell like burning horn; vegetable fibres, on the other hand, produce a smell like that of burning paper.

We have naturally but little to say here about the fibres themselves. The most important things made from animal fibres are wool and silk. Wool has a very rough surface set with many little projections. Woollen cloth is made by stretching woollen threads on a frame, and so forming the warp, on which the woof is spun by a shuttle which flies to and fro; the cloth made in this way is very similar in appearance to stuff made of strong linen fibres. But if the material is now wetted and worked vigorously, or *milled* as the expression is, the projections of the single threads are kneaded into one another—the cloth is said to be *felted* or *fulled*—and the product has the surface we are accustomed to perceive on woollen goods. The processes to which the cloth is then subjected—*shearing*, *teaseling*, etc.—belong to the technical details of the manufacture, and do not interest us here.

The properties of silk do not allow of its being felted; the single threads can therefore be distinguished in finished silken fabrics. This is the case also with linen and cotton.

However much cotton or linen goods may be washed, the single threads always remain side by side, and they can be separated by picking.

But artificial wool, mercerised cotton-wool, and artificial silk are much more interesting to the chemist than the materials that are spun from the natural stuff.

When woollen clothes have become unfit for further use because of constant wear, the greater part of the wool that was used in making them still remains in the clothes; only their appearance is bad—they have gone into holes, etc.

It is easy to see that if woven goods, such as hosiery, are completely picked to pieces—and this can be done without trouble by a machine—a wool will be obtained which may again be spun, and which, although not equal to unused wool, will yet be of some service.

Now it is not only such woollen goods that are picked to pieces, but cast-off wearing apparel, that can be obtained in much greater quantity, is also treated in this way. All the stitches must be taken out of the clothes before they are picked to pieces by the machines. This preliminary treatment is done by workwomen. The odd pieces of cloth thus obtained are sorted, and then pulled to pieces. The wool is thus got out of the cloth; but a little consideration will show that the threads of this wool will be much shorter than those of the wool from which the cloth was originally manufactured. Nevertheless this wool is an excellent material for weaving, and finds a very suitable use in making up those cheap stuffs which are purchased by people that are not well-to-do.

The manufacture of such stuffs would be very easy were it not for the following consideration. Cotton is much cheaper than wool; hence some cotton is generally mixed with wool before spinning, in order to reduce the price of the articles

manufactured therefrom. But as wool and cotton cannot be dyed equally (the reason of this we shall learn later) it is not customary to mix cotton with wool in a casual manner; the practice rather is to make the warp of cotton threads and the woof of wool. When the cloth is milled the wool is mingled with the cotton sufficiently to cover and so to hide the latter.

It is only at those parts of the clothes where there is much wear—at the armholes, for instance—that the wool soon gets rubbed off and the tightly twisted separated threads of cotton make their appearance. If such clothes are again picked to pieces to make artificial wool—known as *shoddy* or *mungo*—the stuff contains cotton, and when the process has been repeated several times the material becomes quite useless.

To make shoddy that contains cotton fit for use the cotton is removed by a process known as "*carbonising*." The stuff is placed in dilute sulphuric acid, or in some other liquid which acts in a similar way. The liquid used attacks the cotton in the material in such a way that after drying at 90° to 95° C. [194° to 203° F.] the cotton is disintegrated to a powder, while the wool is practically unaffected. The cotton can then be completely removed by working up the material in machines.

Mercerised cotton-wool differs from the ordinary material in its silky lustre. The preparation of it is fairly simple. Tightly stretched cotton-wool is immersed in soda-lye (about which we shall learn something in Lecture VIII.), and is then thoroughly washed. The invention depends on the stretching of the cotton; if the cotton is not stretched it shrivels up and is useless.

The preparation of artificial silk, a name applied to various lustrous stuffs, demands much more skill than that of

mercerised cotton. The process consists, in the main, in dissolving cotton-wool, or nitrocellulose made from cotton-wool, in a suitable solvent, and causing the solution to flow from a very fine orifice into a liquid wherein cotton-wool and nitrocellulose are insoluble. A solution of a compound of copper, to which much ammonia has been added, dissolves cotton-wool; we have already seen that there are many solvents for nitrocellulose (p. 128). The threads of the material thus obtained have a very fine lustre, hence the name *artificial silk.* If nitrocellulose is used, the product is a kind of smokeless powder (p. 126); it must be treated with chemical substances which remove the nitrogroups, a process of no especial difficulty. Because of its exceedingly fine lustre, large quantities of artificial silk have been used for decorative purposes.

It is interesting to know that, by forming coarser threads, a very good imitation of human hair is produced, instead of artificial silk. Excellent artificial horsehair has also been made. In the beginning of 1908 twenty-two factories of artificial silk had been established.

Most of the fibres that are spun into materials are colourless as they occur naturally. But as it would not always be convenient to wear white garments the practice of dyeing materials has prevailed since early times.

LECTURE VII

Tanning—Leather—Removing hair from hides and softening them—Tanning materials—Barks—Quebracho bark—Sumac—Tanning extracts—Sole leather—Alum tanning—Glove leather—Furriery—Iron and chrome leather—Chamois leather—Wash leather—Parchment—Bleaching on meadows—Blueing washed linen—Bleaching by chlorine—Bleaching powder—Antichlors—*Eau de Javelle*—Sulphurous acid—*Persil*—Dyeing—Mordants—Lakes—Substantive colours—Coal tar colours—Indigo—Alizarin—Colouring pastes—Colouring extracts from woods—Log-wood—Calico printing.

BEFORE dealing with the subject of dyeing it is advisable to say something about the preparation of leather, which, being the substance that serves as a covering for our feet, naturally finds a place after those materials that are woven from threads and made into clothing. For many other purposes of ordinary life also nothing can be substituted for leather.

Leather is the skin of animals which is so changed, by the process of tanning, that it neither putrifies nor becomes hard when it is dried.

Fresh skins of animals are extremely liable to undergo putrefaction. They lose this tendency when they are dried; but the dry skins are hard and brittle because their fibres are glued together. In the process of tanning the tanning material is brought between the fibres, and so prevents the adherence of those fibres to one another; leather is thus produced the pliability of which is more or less like that of the skins of living animals.

The first thing to be done with skins that are to be used for making leather is to remove the hair from them. The oldest method for doing this is known as "*sweating*"; this method is still used to some extent in an improved form to-day. The process consists in leaving the moistened skins or hides for some time by themselves; a slight putrefaction occurs which so softens the hair that it can be scraped off without much trouble. The sweating is stopped as soon as the hair is softened sufficiently. The process of loosening the hair can also be easily accomplished by the aid of chemicals; and burnt lime has long been used for this purpose. The lime is slaked with a large quantity of water (we shall have to deal with the slaking of lime when we come to speak of mortar), and the hides are steeped in the *milk of lime* thus obtained. A compound of sulphur and lime, or the chemically similar compound *sulphide of soda*, is a more effective depilatory than lime. These substances are now manufactured especially for the purpose of removing the hair from hides that are to be made into leather.

After the hair has been removed the hides are soaked in some liquid which takes away any lime that still adheres to them, because if this lime were allowed to remain in the hides it would interfere with the tanning processes. Very dilute acid—sulphuric acid, for instance—may be used for this purpose; when soaked in such a bath the hides swell up to twice their original thickness, and so become more easily permeated by the tanning materials.

It is, however, customary to employ a method that has been handed down from ancient times, and which is purely empirical. The acid bath is prepared by the process of lactic fermentation, with which we are already familiar; the result is found to be more satisfactory than when the bath is made of any one of the dilute acids that have been tried

for this purpose. The bath is prepared by steeping wheat bran in water, adding sour dough, and allowing the lactic fermentation to complete itself at about 50° C. [120° F.]. As we already know, small quantities of other acids besides lactic acid—butyric acid, for instance—are produced by this process (see p. 85).

When the hides are steeped in this bath, after the liquor has become cold, they swell up and become ready to absorb the tanning substances from the materials used in the next stage of the process.

Tanning substances—that is to say, substances which convert the skins of animals into leather—are found in very many plants. One speaks, for example, of the *tannin* of tea and coffee. The high price of such plants as those that produce tea or coffee of course negatives the employment of these materials in leather making. Barks are the most commonly used materials, and especially the bark of the oak, which, when cut into small pieces, is known as *oak tan*, or simply *tan*. The trees are barked when they are from fifteen to twenty years old, as the proportion of bark to wood is greatest at that period of their growth.

To prevent the unnecessary withdrawal of energy from the soil—which means, as we now know, the uncalled-for removal of inorganic salts—the wood of the trees is burnt on the spot, and the ashes go to enrich the soil. Of course the soil may also be enriched by the use of artificial manures.

The barks of firs, pines, and in many places also the bark of the walnut tree are employed for tanning, besides oak bark; but these are generally mixed with oak bark before use. In consequence of the large quantities of leather that are used nowadays substitutes for bark are derived from other sources, especially from certain foreign trees and shrubs, for the tanning substances are found in other parts of plants

besides the bark. The only one of these woods we shall mention is *quebracho wood*. This is a very hard, dark red wood, which is exported in large quantities from Argentina; after it has been rasped to pieces by a machine it is used in the same way as oak bark.

Sumac is also much used. It is a powder made by rubbing the young dried shoots of plants of the *Rhus* order which grow in the southern parts of Europe. But we need not make any further enumeration of the materials used in tanning.

Tanning with oak bark, or a substitute for bark, is conducted by placing the swollen hides and the tanning material in alternate layers in a pit until the pit is full, and then running in water sufficient to cover the whole of the contents. The tanning substances gradually pass into solution, and they are slowly absorbed by the hides. As thick hides require very large quantities of tanning material, they must be mixed repeatedly with fresh layers of tan; the process therefore occupies a long time, even as much as two years or more; but for that reason the product is excellent.

Naturally attempts have been made to shorten the process; and it has been found possible to complete the making of leather in about three months by extracting the tanning material with water and then steeping the hides in the liquor thus obtained.

This brings us to the consideration of extracts used in tanning. Such extracts have been sent on to the market for many years from the East Indies, where they are prepared by extracting suitable woods or leaves with water, and then evaporating as far as possible so as to decrease the cost of transport; the most important of these extracts are known as *gambier* and *catechu*. Similar extracts have been prepared

in Europe since the year 1882, and the cost of carriage of tanning materials has thereby been much diminished; extract of oak bark, for instance, comes from Hungary and Croatia, extract of chestnut bark from Corsica, and extract of quebracho wood from Argentina and the European seaport towns to which the wood is brought. The manufacture is carried on by rasping or grinding the material, exhausting with water, and evaporating the aqueous solution thus obtained. The evaporation is not effected in open vessels, but under greatly reduced pressure in a way like that followed in making sugar, about which we have already learnt something (see p. 75). This method preserves all the desirable properties of the extracts, which could not be done were the evaporation conducted in the ordinary manner.

The preparation of leather by the use of such extracts is a much less troublesome process than the manufacture by the older methods; and the process is also quickened to an extent that is quite astonishing.

A German patent of 1892 asserts that the thickest sole leather can be made in thirty-six hours, by treating soaked hides with an extract liquor eight times more concentrated than that generally employed, in a machine which revolves about ten times per minute. Instead of requiring a couple of years, as was formerly the case, prepared hides can now be made into leather in less than two days; and this patent is not impracticable, as many patents are, for sole leather made by this method—and it is only for sole leather that the process seems to be suitable—has taken a firm place on the market.

Besides the methods of tanning that we have been speaking of there are two other processes that are much used; these are *alum tanning* and *chamois leather tanning*.

Chemically considered, alum is a double compound of

sulphate of potash and sulphate of alumina. When soaked and cleaned hides are brought into a solution of alum to which common salt has been added, the alumina acts in the same way as the tanning substances do which we have already considered ; the alumina penetrates the hides and by its deposition between the fibres prevents the hardening of the material which is subjected to this tanning operation. When this product is thoroughly rubbed and worked with fat, the fat is taken into the substance, and the material thus obtained is the most tenacious kind of leather that is known.

The leather for kid gloves is made in this way, working with very great care to prevent the formation of spots, etc., and using the skins of young animals, especially those of kids and lambs. The tanning liquor used for this purpose consists of a solution of alum to which egg yolks and meal have been added. Egg yolk consists chiefly of albumen and fat, the latter being present in an extremely finely divided state ; and it is to the thorough permeation of the skins by this finely divided fat, along with the tanning material, that the remarkable pliability of kid glove leather is due.

Although alum or white tanning is not nearly so effectual as tanning by oak bark, nevertheless there are many purposes for which the latter cannot be used. The leathers made by these two methods show great differences in their behaviour towards water. Experience in the wearing of boots shows us that good sole leather is impervious to water ; but the tanning matter is nearly all withdrawn from white tanned leather by the action of a large quantity of water. We know, for instance, that when gloves get very wet they shrivel, and behave like untanned skins.

Alum is also employed in the tanning of skins to be used as furs. The details of the various processes differ much

but the method is essentially a tannage by fat and alum. Speaking generally, the skins are thoroughly cleaned with soap, then dried, and then fat is rubbed on to their inner sides and worked in as thoroughly as possibly and as long as any of it is absorbed; the skins are then placed in a sour bran-drench, which causes a slight swelling after about twenty-four hours; the bran is then removed, and the tanning is effected by a solution of alum and common salt.

Alumina is a base (see p. 49); hence it does not seem absurd to suppose that other bases might be substituted for alumina in tanning, and that new kinds of leather might thus be produced. A consideration of the properties of various bases by experts led to the conclusion that there are only two which would be worth trying, and these are oxide of iron and oxide of chromium. As a fact leather has been prepared by using these bases; but only the second has continued to be used. Chrome leather is soft and supple; and as it is more impervious to moisture and resists high temperatures better than other sorts of leather, it has come into lasting use. Indeed, in 1908 the three largest German makers of upper leathers announced that they would not require any more oak-bark.

We have still to speak of *chamois* or *oil tanning*. Here also the skins are freed from hair, and are swollen; they are then rubbed with fat, fish oil or whale oil being the form of fat that is used, and afterwards they are thoroughly fulled, and are again rubbed with oil as long as any is absorbed. The absorption of the oil is not altogether a mechanical process; a chemical change also occurs, and this is accompanied by the production of a definite smell which indicates that the operation is completed. The skins are then allowed

to remain for some time in heaps, where they become warm owing to the heat produced by the chemical changes that continue to occur; the rise of temperature favours the chemical reactions, which proceed more rapidly until at last the skins acquire a yellow colour. The result of this treatment is that the fibres become so enveloped in fatty matter that they no longer adhere together—a true leather is produced—and the combination of the fibres with the fat is so intimate that even hot water is not able to dissolve it; for this reason the leather is called *wash leather*. The leather is then washed with potash solution to remove the surplus fat that remained chemically uncombined when the yellowing of the skins began. This fat forms an emulsion with the potash, and is removed by washing with water. If the potash in the emulsified liquor is neutralised with acid the fat rises to the top of the liquor. This fat is found, by experience, to be very suitable for rubbing into leather prepared by the methods of tanning described in the earlier part of this lecture; it comes into commerce under the name of *degras*.

Furs are also sometimes prepared by the methods used in making chamois leather.

Parchment should be mentioned here. Although parchment is often supposed to be a leather, yet it is not; it is prepared by removing the hair from the skins of very young animals by means of lime, then cleaning the skins thoroughly and drying them while they are stretched tightly. To give the dried skins a smooth surface they are sprinkled with chalk and rubbed with pumice stone. The product is too smooth for writing on, and therefore, if it is not to be used for binding books, making drums, or some such purpose, it is brushed over with thin white oil paint so as to produce a surface that can be written upon.

We must now return to textile fabrics that we may consider the bleaching and dyeing of these materials. In connection with dyeing we shall have something to say about painting. White, or nearly white, is the natural colour of the materials that are woven in linen, cotton, and woollen goods, and the like.

It would not be altogether pleasant to wear white clothes, because their appearance soon becomes disagreeable ; besides this, coloured stuffs confer a more beautiful and more distinguished appearance, as was recognised in the olden days when a red-purple mantle was worn only by the chief men. Careful investigations, made since 1908, of the shellfish from which purple dye was obtained by the ancients have shown that the purple then used must have had a rather disagreeable blue-black tinge.

Most of the natural materials that are woven have a shade of yellow in them, and the object of bleaching these materials in the sunshine is to remove this colour. This yellowish coloration is removed, as most colours are, by exposure to sunshine ; the process whereby the yellow is changed into pure white is hastened by blueing the goods—this is practised with the household washed linen, for instance. Yellow and blue are complementary colours, and they neutralise one another.

When, in course of time, the making of linen and cotton fabrics passed from the hands of individual home-workers, and the manufactures became concentrated in factories, it was necessary to provide very large bleaching grounds for the goods, and this involved much trouble and expense. In some districts, indeed, where the manufacture of these goods has advanced very much, it would be quite impossible to provide sufficiently large bleaching grounds. Nowadays, and indeed since the discovery of artificial bleaching stuffs, all

linen and cotton fabrics are bleached in the factories, by the use of chloride of lime.

Chlorine is a gas which shows a very marked readiness to combine with other bodies. It was not until some time after its discovery, in the last quarter of the eighteenth century, that this substance was recognised to be a distinct elementary body. Because of its great activity—an activity greater even than that of oxygen, which was the most active substance known at the time of the discovery of chlorine—the gas was supposed to be a new kind of oxygen, and the French chemists of that period often spoke of *nouvel oxygène*. In consequence of its energetic action on the most different kinds of substances, chlorine destroys the greater number of colouring substances.

The employment of gaseous substances in factory industries is very inconvenient; for this reason chlorine is not itself used as a bleacher, but the compound is employed which chlorine forms with lime when it is passed over that substance. This compound, which was first prepared in 1799 by Tennant in Glasgow, is known as *chloride of lime* [or as *bleaching powder*]. At first, 1000 kilograms of bleaching powder cost 2800 marks; in 1820, only 540 marks; and at present, about 110 marks. [About £140, £27, and £5 10*s*. per ton.] When bleaching powder is shaken with water, the insoluble parts of the powder sink on standing, and a clear solution of the bleaching substance is obtained. If lime is added to this liquid, and chlorine is passed into it, *crystallised chloride of lime* separates. This substance has become a commercial product since 1907; it is much more effective than ordinary bleaching powder.

The bleaching action, or, to use a more accurate expression, the chemical energy, of this substance destroys the yellowish tint of white linen or cotton goods in a very short time, and

as effectually as the process of bleaching on meadows. But the energy of the bleaching powder is not exhausted by this process; having destroyed the colour, the bleaching powder attacks the fibres of the goods—and it is for this reason that the use of bleaching powder has never found favour with housewives. In factories, however, matters are managed differently; as soon as the goods are bleached the excess of chlorine is rendered inactive by addition of an *antichlor*, and the fibres of the goods are not injured in the slightest. Many and very different chemical substances may be employed as antichlors; the most commonly used is *hyposulphite of soda*. This salt has no action on washed linen, and as soon as it comes into contact with chloride of lime it forms new compounds which are also without action on the linen, and at the same time the chloride of lime is converted into the perfectly harmless chloride of calcium.

In addition to chloride of lime, the substance known as *eau de Javelle* is used commercially as a bleaching agent. The difference between these two substances is that the eau de Javelle contains soda in place of lime; the chemical action of the one is practically the same as that of the other. If eau de Javelle is used—and it is in favour for removing stains, which it gradually destroys—a small quantity of an antichlor—a little hyposulphite of soda dissolved in water, for instance—should be put on the cloth after the cleaning has been effected, as if this is not done the fibres will be rotted.

Chloride of lime cannot be employed for bleaching fabrics woven from animal fibres, because it does not thoroughly bleach such fabrics, but only turns them yellow. *Sulphurous*

acid, which is a less energetic bleaching agent than chloride of lime, is employed for taking away the colour from animal fabrics.

Sulphurous acid is the sharply smelling gas that is formed when sulphur is burnt. As the gas is very soluble in water, the usual method of working is to hang the goods, after wetting them, in a chamber wherein sulphur is burnt. No special means of destroying the excess of sulphurous acid is required, because, when this method is adopted, only a very little sulphurous acid ever gets into each piece of goods.

We have still to mention *hydrogen peroxide*. The word *peroxide* tells that the compound contains much oxygen. It is to the excess of oxygen that the bleaching power of the substance is due.

This substance can be used as a bleaching agent in many cases where chloride of lime and sulphurous acid are ineffectual: it is employed especially for bleaching hair, feathers, and ivory. Of late years peroxides have been more widely used for bleaching. For a time, a mixture of sodium peroxide, soap, and soda was employed; but this has been superseded by *Persil*, which contains 10 per cent. of boron peroxide. By mixing persil with the liquor in which white goods are washed, the goods are at once washed and bleached. Persil, however, quickly destroys some of the colours of dyed cotton and woollen goods. It is only since the introduction of the electric current into manufacturing chemistry that it has become possible to prepare peroxides cheaply.

We have now to consider the dyeing of textile fabrics. This part of the subject falls into two main divisions: the uniform dyeing of the whole of a piece of goods, and calico printing.

The simplest way of dyeing uniformly a piece of cloth would be to mix the colour with glue in water and to smear this over the goods; but the colour would be very loosely retained, and the cloth would have to be protected from wet. Cloth treated in this way would rather be described as coloured than as dyed: the colour is retained better if it is mixed with albumen and spread over the cloth, and the cloth is then heated; the albumen is coagulated, and is thus rendered insoluble in water. Although the colour is fairly well held by the cloth, still much of it is removed when the cloth is rubbed vigorously.

This process, which is not a dyeing process in the proper meaning of the term, plays a certain part in calico printing. It is applicable only when a solution of the colouring matter acts upon the fibres of the material. There are great differences in this respect; animal fibres, such as wool and silk, behave towards dye-stuffs very differently from vegetable fibres, of which cotton is the most important.

If a dye-stuff, say *fuchsin*, is dissolved in water, and a piece of wool or a piece of silk is drawn through this solution, the colouring matter slowly passes from the solution into the fibres, which it colours red.* But if we place cotton in the same solution we find that the vegetable fibres have not the property of retaining the colouring substance. For if we now wash the red coloured wool or silk with much water the colour is still retained by the material; but when the cotton is treated in the same way it returns to its original whiteness.

All dye-stuffs cannot, however, be applied to wool and silk so easily as this. In wool and silk dyeing it is generally

* The fibres play here somewhat the same part as we found was taken by animal charcoal (see p. 42). In the same way as animal charcoal withdraws the colouring substances from liquids—from red wine, for instance—animal fibres are able to combine with colouring matters and to retain these firmly.

necessary to make use of the method which was the only practicable method for dyeing cottons till the year 1884; it is necessary to use *mordants*. What mordants are will be best understood by the following considerations.

If a solution containing iron is added to a solution of yellow prussiate of potash the beautiful blue substance known as *Prussian blue* is precipitated. Now the best way of dyeing a cloth with Prussian blue is to dip the cloth first into one of the two solutions and then into the other. If the cloth has been soaked in the iron solution before it is immersed in the solution of yellow prussiate, then the blue precipitate is formed in the fibres of the cloth, that is to say, the colouring matter is deposited in the interior of the cloth, and as the precipitate is quite insoluble in water it is not removed by washing even with much water, and hence the cloth is not decolourised. The fabric is really dyed by this process.

The use of mordants is based on such a process as that which has just been described. The stuff to be dyed is first dipped into a liquid called the mordant, which introduces into the fibres of the cloth a substance that reacts with the special dye-stuff to be used and produces a compound which is insoluble in the mordant.

Alumina is very much used as a mordant. In dealing with tanning (see p. 141) we found that alumina is able to enter into combination with animal fibres; in a similar way this substance shows a tendency to combine with both animal and vegetable textile fabrics when these are passed through a properly prepared solution of it.

Alum, which is a double compound of sulphate of alumina and sulphate of potash (see p. 141), was formerly a very important substance in dyeing, inasmuch as it was the

only soluble salt of alumina that was also easily procurable. This compound has been prepared since ancient times by an easy process from a kind of earth which is found in certain parts of Europe. As the sulphate of potash in alum is useless for the purposes for which the alum is to be employed in dyeing, chemistry has long ago replaced this double salt by various other soluble compounds of alumina.

Now if cotton, for instance, is mordanted by being dipped into an alumina solution, and if it is then passed through a solution of fuchsin, the fabric is dyed a fast red ; for the fuchsin is deposited in the fibres of the fabric in the form of an insoluble compound with the alumina, and the process is quite similar to what occurred when we dyed with Prussian blue.

The name *lakes* is given to the compounds that mordants form with dyes. Of course we can produce a lake without using fibres : for instance, if we pour a solution of fuchsin into a solution of alumina a red precipitate is obtained ; and if we dry this lake and then rub it up with varnish (see forward, p. 161) we have a colour ready for painting wherewith we can cover surfaces in any way we desire.

Alumina is a base, and there are many other bases that may be used in dyeing in the same way as alumina is used. Matters are different here from what we found them to be in leather making, where alumina was almost the only practically useful base (see p. 141). It is not only the bases that we are all familiar with, oxide of iron and oxide of chromium, that play important parts as mordants, but there also are a great number of other oxides suitable for holding fast the dyes in the fibres of fabrics. There is, for instance, oxide of tin, which is used in the form of a solution of chloride of tin, or as it is commonly called *tin composition.*

Tin is not a very cheap metal to-day, and in former times it was extremely costly. Nevertheless this metal began to play a great part in dyeing after the discovery, made accidentally in 1640, in Holland, that the most beautiful scarlet the world had seen was produced by dyeing with cochineal after mordanting with a solution of tin ; and the importance of tin increased when it was found at a later time that it had the property of increasing the brilliancy of many other dyes. Although more beautiful scarlets have been dyed in the last thirty years or so by the use of aniline colours than could be obtained from cochineal, nevertheless tin has retained its importance in the dyeing industries because it is an extremely suitable reagent for fixing the most different kinds of dyes.

Besides the metallic oxides which are precipitated in the fibres of goods, and concerning the chief of which we have now learnt something, there is another important mordanting material known as *tannin*.

Tannin forms lakes directly with solutions of various dyestuffs, so that goods can be dyed with the help of tannin. In addition to this, goods that have been treated with tannin are sometimes passed through solutions of alumina or other similar oxides; compounds of tannic acid with alumina (or the other oxide) are thus formed in the fibres, and if after this double mordanting the goods are dipped into various dyeing solutions, lakes are formed that are composed of tannin, metallic oxide, and the dye. With the help of tannin most remarkable results can now be obtained.

We said above that no practical method for dyeing cotton goods without using mordants existed before the year 1884, and that however simple may be the theory of mordants the process of dyeing by their use requires much practice. For

instance, it is a very difficult matter to fix the celebrated red dye known as *Turkey red* on cottons. This kind of dyeing is especially distinguished from others by the fact that oil must be added to the mordants that are to be employed. The mordanted fabric is dyed in a bath of *alizarin*, a dye-stuff to which we shall return again. This process of dyeing has been long known in the East; but it has been fully developed only in Europe, and the cotton goods dyed in this manner in Europe have overrun the East. Enormous numbers of handkerchiefs, more especially, dyed in this way are sent to the Eastern markets.

This industry was naturally much menaced when a new red appeared in the year 1884, called *congo red*, which dyed cotton directly. Suppose an Indian woman wants a red cloth, she need only dissolve a little congo red in water, soak the piece of cotton in the liquid for a short time, and then draw it out dyed red. This red it is true is not nearly so fast as Turkey red; but that does not matter, as a repetition of the very simple process will bring the cloth back again to the desired colour. Colours which will dye without the employment of mordants are called *substantive colours*. Congo red was the first cotton-dyeing substantive colour known; it has been followed by very many others of all varieties of shades.

Substances known as *diazo compounds* have long played an important part, as intermediate products, in the chemistry of the colours obtained from coal tar. Compounds of this class are extremely ready to enter into chemical change; and while people were engaged in one place in experimenting on the applications of colours prepared by the help of these compounds rapid advances were being made in other places. Compounds can indeed be obtained which contain the diazo group twice, and which must be still more chemically energetic than their analogues that are but half as richly

endowed as they. Individual bodies of this kind have long been known to science, and they have been employed in purely theoretical investigations. The examination of those substances that bear the class names *bisdiazo*, and *tetrazo*, *compounds* for the purpose of finding whether they were capable of technical applications, led to the discovery of those colouring matters that dye cotton directly.

Lack of preliminary knowledge makes it impossible for us to go deeply into the consideration of the *coal tar colours*, or, as they are generally called, the *aniline colours*. Indeed this lecture will be fully understood only by those who have a wide and full chemical knowledge. It should be stated clearly that these colours are not coal tar colours in the sense wherein this term is generally used by the public. Tar, that thick, black mass, cannot be worked up directly into colours.

The coal tar is first of all distilled; for this purpose we may employ an apparatus like that we made use of in distilling wine (see p. 25). When the tar is heated in such an apparatus, clear water-like oils pass over for some time, just as spirit distilled over from the wine. These oils form a part of the material from which coal tar colours are manufactured; after these oils, distillates come over which partially solidify on cooling. *Carbolic acid* is obtained from these, and later on also *naphthalene* and many other bodies, among which we need mention only *anthracene*, as that is a substance we shall have to speak of again. If the process of distillation has been carried on long enough a solid mass resembling coke, which can be used for burning, remains in the distilling vessel.

Before considering alizarin, which is the most important colouring matter derived from anthracene, we must speak of

indigo. This blue dye has been known from the remotest times, and has been made from the juices of several nearly allied plants which grow in India; the juice is itself colourless, but when it stands in the air a process of oxidation occurs and indigo separates. As indigo is a beautiful blue colour, and as it resists the action of light and air, of acids and alkalis, and of substances used in washing, it may well be called the king of colours.

There is a European plant called *woad*, from whose juice indigo separates on standing; but the quantity of indigo so obtained is only about three-tenths of a per cent., which is very much less than the amount obtainable from the Indian plants. In olden times, however, because of the slight connection between Europe and the East, woad was used exclusively in Europe; and as there was a very considerable demand for blue dyes the trade in woad-blue reached considerable dimensions in some districts, and led to the amassing of large fortunes.

In the year 1300 there was a large trade in the neighbourhood of Erfurt, where those burghers who alone had the right to grow woad were known as *woad burghers*. Even as late as 1600 several hundred villages in Thuringia were occupied in the cultivation of woad. But at last the trade could not compete with that in the cheaper Indian indigo, although both Princes and States attempted to save it, not only by imposing protective duties, but also by prohibiting the importation of indigo. The Nürnbergers, for instance, were long accustomed to swear to their fellow-townsmen every year that no foreign indigo would be used in their manufactures. Until recently Indian indigo controlled the markets of the world; but it will not continue to do this much longer. In the first place blue dye-stuffs have been prepared from tar which are able to compete with indigo; and in the second

place the problem of the artificial preparation of indigo was completely solved in 1880 by a series of wonderfully penetrating researches by von Baeyer. The preparation of indigo by these methods, starting from coal tar, at present, however, costs more than the price of the natural substance. But many other methods have already been worked out for the synthesis, that is, the artificial production, of indigo ; and, as a result of work which had been going on for seventeen years artificial indigo was placed on the market in October, 1897, at a moderate price. The peasants of far Bengal must use their fields for the cultivation of other plants. In 1897 there were 500,614 acres devoted to the cultivation of the plants which yield indigo ; in 1901 the acreage was 160,890. Whereas India produced about 3½ million pounds' worth of indigo in 1894, the value of the indigo produced in 1904 was about £500,000. The quantity of artificial indigo used by the world to-day amounts to about 85 per cent. of the total consumption.

As regards indigo, although on the one hand it is true that the improved relations of trade between India and Europe have driven out of cultivation in this part of the world a European plant which yields a dye, yet on the other hand we know that the advances made by chemistry in the production of dyes in the laboratory, and in connection therewith in factories also, during the last fifty years, have made the cultivation of another similar plant unprofitable in any part of the world.

This has been the case with *madder*, with which very different colours, but more especially a very beautiful red, can be dyed. This plant was cultivated throughout the whole of Southern Europe as far north as Baden, and also in Asia Minor, and in other places. The roots of this plant were used in dyeing, and these were known in the

East by the name *alizari*, from which our word alizarin is derived.

These roots contain a number of dye-stuffs. Although very painstaking investigations into the chemical nature of these substances had been in progress since about 1823, the difficulties of the inquiry proved so great that but little advance was made for many years. It was not till the year 1868 that the connection was established between alizarin, which is the chief dye-stuff in madder roots, and the hydrocarbon anthracene which is contained in coal tar. At a later time alizarin was shown to be chemically a *dioxyanthraquinone*; and this knowledge led to a method for converting anthracene into this dioxyanthraquinone. At once all the energies of the trade were devoted to the preparation of this dye-stuff.

The methods that were at first made use of in the laboratory were found to be unsuitable on the large scale, hence these methods had to be replaced by others; but, after the expenditure of much labour, the manufacture of artificial alizarin has at last become so perfect that it can hardly be improved upon, and the natural product is no longer able to compete with the artificial substance in the matter of cheapness. As a consequence of this, madder is no longer cultivated in any part of the world.

It has already been mentioned that a series of colours can be obtained in dyeing with madder, and also with alizarin; the final colour depends on the mordant that is used. Alumina mordants produce red dyes; iron mordants give dark tones, passing into black when much iron is used; chrome mordants dye violet, and so on. Very remarkable results can be obtained by the use of alizarin. If, for instance, a piece of cotton goods is soaked in different mordants successively, hardly any change is made in the appearance of the cotton when it is dried. But if the material

is now dipped into boiling water wherein a little artificial alizarin—which is a yellowish paste—has been dissolved, and, after remaining there for a little time, it is then washed in much water, the cloth shows a complete scale of colours.

Alizarin comes into commerce in the form of a paste which contains a large quantity of water, because dried alizarin is but slowly dissolved by water.

We have still to mention the extracts from woods that have been introduced in recent times into the dyeing industries. Aqueous extracts of various woods, such as log-wood or Brazilwood, produce colours on mordanted fabrics and are therefore useful for dyeing purposes. In order to save cost of transport these aqueous extracts are generally concentrated by evaporation (in the same way as was described under tanning extracts, p. 139) at the seaport towns, and the dyer uses the concentrated extracts thus prepared.

The coal tar colours are dangerous competitors against these extracts, and it is not unlikely that they may drive the extracts out of the field. At the present time more than four hundred different coal tar colours are used in dyeing, and the most varying shades of colour are obtained from these by using different mordants. But that number is very small compared with the vast array of colours of this kind that has been prepared. But the demands for fastness in colours, as regards the action of light and washing, have become so much more stringent of late years that it is only those colours which completely satisfy these demands that have any chance of finding technical applications.

Finally a word must be said regarding dyeing goods in designs. The custom used to be to imprint the designs directly on the goods. Then the method was discovered of

covering the parts which it was desired should remain undyed with some substance that was not permeable by the dyeing solution. Such a substance was generally prepared by melting together resin and wax; when patterns had been stamped on the cloth with this material the whole was dipped into the dyeing bath, and the goods came out showing white patterns on a coloured ground. This was followed by the method of printing the patterns; the designs were cut in wood, the wood was covered with the colouring matter by the use of a cloth on which the colour was spread, and the wood was then pressed down upon the goods. The method was practically the same as that used in everyday life for imprinting a name cut in a stamp (which is nowadays generally made of caoutchouc) on to paper.

Calico printing has, however, for many years made use of machines, which have now been brought to great perfection. There are automatic machines in use to-day which are able to imprint sixteen different colours in succession on the same fabric.

LECTURE VIII

Oil-painting—Drying and non-drying oils—Linseed oil—Varnishes—Inks—Cellulose—Paper—Sizing paper—Straw boiling—Esparto grass boiling—Soda cellulose—Sulphite cellulose—Silvalin.

THE process of printing designs on goods, which we spoke of at the close of the last lecture, leads us to consider painting itself, wherein prepared colours are mixed with such a vehicle as size and are then laid on to the surfaces that are to be coloured.

What are called *water colours* are fairly satisfactory; but they leave much to be desired, especially because they cannot be used in the open air, as if they get wet the colours run.

In the last few years the easily prepared aniline colours have been used in painting, whether with water colours or in oils, whereas formerly only mineral colours were employed.

These colours are affixed to a basis of some kind by the help of an oil. Suppose, for instance, that a brick has been ground to very fine powder; this powder will represent an almost indestructible red colouring material. No one would use this particular colouring matter, because it is not sufficiently beautiful; but coloured materials are found in nature, or are prepared by strongly heating or melting different substances,

which can be made ready for use in painting by grinding in the same way as was done with the brick. If, for instance, cobalt compounds are added to glass during the manufacture, and the resultant blue mass is finely ground, the extremely stable colouring material called *smalt* is obtained. Again, many of the precipitates that are formed when solutions of two salts are mixed are available as colours; yellow chromate of lead, for instance, which is used under the name of *chrome yellow*, is prepared by mixing solutions of chromate of potash and acetate of lead.

The following points are to be noted in connection with oil painting. Oil colours cannot be prepared with all kinds of oil. If the colours were rubbed up with olive oil, for instance, the products would not dry, as olive oil leaves what are called fat spots—that is, spots which never completely dry up.

The oils fall into two main classes—drying and non-drying oils.

The chief constituents of the non-drying oils, including olive oil, are two substances about which we already know something (see p. 19)—namely, oleic acid and glycerin; and this oleic acid is identical with that which enters into the composition of such animal fats as ox tallow. In the drying oils oleic acid is replaced by other acids the names of which are generally derived from the names of the oils in which they occur; linseed oil, for instance, which is one of the drying oils, contains *linoleic acid.* *Linseed oil* is obtained by pressing linseed. We know that seeds contain large quantities of oil (cf. p. 60); linseed [seed of the common flax] is especially rich in oil, about 22 per cent. of oil being obtained when the seeds are pressed cold, and about 28 per cent. when they are pressed hot.

Neither kind of oil can be kept for a long time in the air without undergoing change. Olive oil and similar oils become rancid, and the drying oils change into hard, transparent masses, especially if they are spread out in thin films. When an oil becomes rancid there is a partial decomposition into free fatty acids and glycerin; these changes are thought by some to be brought about by moist air alone, while others suppose that the presence of a bacillus is also necessary. The solidification of the drying oils depends simply on a process of oxidation, whereby linoleic and similar acids are completely changed.

It should be noted that some oils, such as cotton-seed oil, contain both ordinary oleic acid and another, drying, oleic acid. Such oils are distinguished as badly drying oils, a name which explains itself.

It is a very remarkable fact that the drying oils dry distinctly more rapidly when their oxidation is started artificially—when they are boiled, for instance, with a substance such as lead oxide which gives up oxygen. Linseed oil which had been boiled with lead oxide was used for rubbing with colouring materials to form the oil colours that were used in painting in the fourteenth century.

Linseed oil, the oxidation of which has been started in the manner described, may be spread over any selected surface, which may or may not have been already treated with water colours; the oil then dries to a very hard, glassy, transparent skin, and the surface is said to be varnished.

The term *varnish* has, however, a somewhat wider signification. The term is taken generally to mean, not so much boiled linseed oil, as solutions of resins in that oil or in some medium which readily evaporates. Such solutions in very volatile media are sometimes called lakes [in Germany].

A solution of *shellac* in alcohol is used as a varnish which dries very quickly, as the spirit rapidly evaporates when exposed to the air. Spirit varnishes are, however, looked on with less favour than solutions of resins in turpentine oil, because the thin coatings which remain when the latter evaporate are much firmer than those left by spirit varnishes.

The most lasting varnishes are obtained by dissolving *amber* or *copal* in boiled linseed oil. Amber, which is a fossil resin, must be melted before being dissolved, as raw amber is insoluble in boiled linseed oil. Copal is also a resin. Many plants contain characteristic liquids which flow from the plants, either spontaneously or when the plants are cut, and become solid on standing in the air; these solidified masses are called *resins*. The copal of commerce is obtained from a great many different trees that grow in hot climates. Small quantities of it are also dug from the ground on the east coast of Africa; some say that this copal is a fossil, others that it has exuded from the roots of plants.

Linoleum is made by boiling oxidised linseed oil with finely ground cork, and spreading the mixture on linen.

We must now consider that coloured fluid which is used more frequently than any other, namely, *ink*. (The name is derived from the Latin *tinctum* = coloured.) The old-fashioned black ink is a compound called *gallotannate of iron* suspended in water. It is prepared by adding a solution of sulphate of iron to an aqueous decoction of galls. A little gum solution is always added, to make the ink of a better consistence for writing, and also to secure the more complete suspension of the black precipitate.

The manufacture of inks has been made much easier by the discovery of aniline colours that are soluble in water. Black ink is obtained by dissolving *aniline black* or *indulin*

black in water. A solution of fuchsin forms a red ink, and a more beautiful red ink is obtained by dissolving *eosin* (ἠώς = the morn) in water. Ink for manifold writing is prepared by dissolving 1 part aniline violet in 300 parts of water, and adding gum solution, etc. Copying inks differ from ordinary inks only in that the former contain more gum and also some sugar; so much of the ink then adheres to the paper which is written upon that a readable impression of the writing can be obtained in the copying press.

We shall mention here the so-called *sympathetic inks*, although these play a more important part in exciting the fancy in romances than in real life. If characters are written on paper with a dilute solution of yellow prussiate of potash, nothing is to be seen when the writing becomes dry, because the salt has only a very slight yellow colour; but if a person who is in the secret brushes the pages over with a pencil dipped in a dilute solution of chloride of iron the writing stands out vividly in blue letters, because the two substances have reacted to produce Prussian blue (see p. 149). It is possible in this way to cause writing to appear in almost any colour by a proper choice of two liquids which react together to produce dark coloured precipitates, but either of which is colourless or nearly colourless when taken alone.

The true sympathetic ink should, however, be more secret than this. In the cases we have spoken of the writing remains legible once it has been developed, but what is desired is that the writing should fade away after it has been read by the recipient of the letter. Such an ink is generally made from a solution of chloride of cobalt or of chloride of copper. A solution of the first of these salts is almost colourless, and writing traced with it is invisible on white

paper. But if the paper is warmed the compound gives up water which it has been holding in chemical combination, the deep blue anhydrous chloride of cobalt is produced, and the writing is very plainly seen. The writing disappears again as the paper cools, because enough water is absorbed from the moist air to cause the re-formation of the colourless hydrated compound. If the writing is done with a solution of chloride of copper, which solution has only a very slight bluish colour, and the paper is afterwards warmed, the written characters come out in a yellow-brown colour, and they vanish again on cooling for the same reason as holds good in the case of chloride of cobalt.

We shall meet with an insoluble ink when we are describing the process of photography.

We must now proceed to the subject of *paper*.

In the oldest times the only materials used for writing on were those furnished by nature, such as stones, pieces of wood, or skins; but the Egyptians very long ago discovered how to prepare paper from the *papyrus* plant. The stalks of that plant were cut into as thin and wide leaflets as possible, and these were placed side by side; a second layer of similar pieces was arranged transversely over the first, and the whole was placed under a press, where it dried together to a single sheet. This was then rubbed as smooth as possible and was ready for writing on.

Besides this writing material, parchment (see p. 143) was used by the ancients and in the earlier Middle Ages, until what we now call paper was discovered in the eighth century. The most ancient European documents written on paper are Papal bulls of the eighth and ninth centuries. The paper seems to have been made by the Moors in Spain, as the oldest deed written on paper made from linen is a treaty of peace

between Castile and Arragon. The paper we use nowadays consists of thin layers of very strongly felted vegetable fibres; fibres from animal sources are not suited for this manufacture.

That paper might be made cheaply, it used to be the custom not to make direct use of the fibrous material as it came from the plants, but to employ in the manufacture the vegetable fibres in the rags that remained when linen and cotton goods had become worn out by use.

Accurate investigations have shown that all vegetable fibres consist of cellulose and other substances which surround, or incrust, the short fibres of the cellulose.

Pure cellulose is a carbohydrate (see p. 66); it consists of six atoms of carbon, ten atoms of hydrogen, and five atoms of oxygen [or a whole multiple of these numbers]. The composition of cellulose is the same as that of starch.

The manufacture of paper was originally conducted as follows.

Wet rags were allowed to semi-putrefy for two or three days, whereby the substances that incrust the cellulose were so far dissolved that, when the rags were boiled with water and a little lime, and were then beaten in the presence of much water, the short fibres of the cellulose became sufficiently apparent. The pulp that was thus obtained was then thrown on to a fine sieve which was shaken to and fro by a workman. The greater part of the water drained off through the sieve, and there remained a thin felted layer of cellulose fibres formed by the interweaving of the single fibres. This was at once removed by a second workman to a thick felt, where it was covered with another similar felt; and when a sufficiently thick pile had been built up, the whole was placed under a press, in order to remove as much water as possible, and

at the same time to give solidity to the individual sheets of paper. The sheets were then taken out of the felts and were thoroughly dried.

Paper made in this way has a loose texture like blotting paper. It can be used for printing on or as packing paper; but it is not suitable for writing on, because the ink is absorbed and spread by the little fibres, and the writing runs. Paper made in this way is also not at all durable.

In order to give greater consistency to such paper, and also to fill up its pores, it is submitted to an operation called *sizing*, a term which does not accurately express the operation in question. For if size were added alone to a paper pulp containing much water, most of the size would go into solution, and would pass through the sieve, and only an insignificant residue would remain in the finished paper. But if alum is added besides size to the paper pulp a different result is obtained. In considering both tanning and dyeing we have learned to recognise the great affinity that alum has for fibres. Here also the same cause is at work; the fibres of the paper hold the alumina, and that in turn prevents the removal of the sizing material. When both alum and size have been added to the paper pulp, then the washing in the sieve does not remove the size, as it is held in the fibres of the pulp by the alumina. When the paper is now dried the fibres adhere together, and a paper is produced which can be written on, as the fibres have lost their capillarity; the size in the paper being insoluble in water also makes the paper less sensitive to the action of moisture.

The surface of paper prepared by hand on a sieve cannot be very smooth; hence all hand-made paper must be glazed after it is made, in order to give it a good appearance. For this purpose the paper is either pressed when moist between flat surfaces, or it is glazed by passing between two highly

polished rollers whereby it acquires a perfectly smooth surface. Hand work in paper making has been gradually and completely replaced by machines; and while formerly the single sheets could not be larger than the largest sieve that a single workman was able to manipulate, the machines produce sheets of very considerable width and of any length that may be desired.

In making paper pulp from rags it is not now the custom to beat the rags after a slight putrefactive change has taken place in them. The rags are nowadays prepared as far as possible for disintegration by boiling with a strong alkali—caustic soda, with which we shall become better acquainted when we come to the soda industry, is used; they are then placed in a rectangular vessel in which revolves a roller set with knives which pass near stationary knives fixed in the sides of the vessel. Such an apparatus, called a "breaker," with its rollers driven by mechanical energy, reduces the rags to a state of a fine division, and grinds them up with water to a pulp.

This pulp is then bleached by chloride of lime, and the harmful after-effects of the bleaching material are neutralised by the use of an antichlor (see p. 146). The next thing to be done is the sizing. Glue is not now used for sizing machine-made paper; but suitable resins (which are much cheaper)—colophony resins, for instance—are boiled with caustic soda lye, and the soaps thus produced (see *soap* in the next lecture) are added, along with alum, to the pulp. The alumina of the alum being held by the cellulose, fixes the constituents of the resins, and these bind together the fibres in the paper, and so make it suitable for writing on.

The pulp which is now ready for making into paper is caused to flow on to an endless wire cloth, made of fine brass

wire, care being taken to dilute the pulp to the proper consistency by a plentiful supply of water; the wire cloth is caused to travel constantly in one direction by means of rollers. A vibratory motion is at the same time communicated to the wire cloth, for the purpose of aiding the felting of the short fibres of the pulp; and any design that may be woven into the wire cloth appears as a water-mark in the finished paper. The paper pulp from which most of the water has already drained off is now seized by an endless felt which carries the pulp with it; a second travelling felt soon meets the first, and the pulp is pressed between these by a pair of rollers, and is thus nearly dried. The pulp now passes on to a polished cylinder which is kept hot so that the paper is dried and at the same time receives a perfectly smooth surface; a second cylinder serves to impart an equally glossy appearance to the other side of the paper. Finally the machine makes up the finished paper into rolls.

It has been found impossible for many years to manufacture from rags alone sufficient paper to meet the enormous demand. A consideration of the great number of newspapers published in these days shows how impossible it would be to make paper enough from that single source; and it must be remembered that much less waste linen or cotton is obtained from each individual than corresponds to the consumption of cellulose per head, be it for writing paper or paper for printing newspapers on. The paper-making industry has been growing of late years more rapidly than any other large industry. As early as the eighteenth century export duties were levied on rags in many countries—in Prussia, for example—in order to make it easier for the home factories to obtain supplies of this material. But a measure of that kind was not of itself sufficient to cause an increase in the supply; and so the

paper-makers began to look about eagerly for a suitable substitute for rags. The result has been that the great advances made in chemical knowledge enable many paper factories to be carried on to-day without using any rags at all.

A little consideration shows that it is very likely that cellulose should be found in many other plants besides in that from which linen is made. But it is possible that although the chemical composition of cellulose from different sources may be the same, nevertheless the physical properties of the celluloses may differ (cf. what was said about starches on p. 67). When straw is properly treated it yields a cellulose ; and a very convenient form of cellulose is obtained from *esparto grass*, which is a plant that grows wild in North Africa, especially in Algiers.

It is to be noted that although every tree, and therefore every kind of wood, must contain cellulose, nevertheless the attempts that were made to manufacture paper from wood were not very successful until recently. It happens that wood was the substance tried in the earliest attempts to find a substitute for rags.

As far back as 1765, Pastor Schëffer of Ratisbon proposed to use macerated wood for making paper. The observation of the nests of wasps led him to suggest the substitution of wood fibres for rag fibres. But the realisation of this idea was not accomplished until 1846, in which year a process of wood grinding was introduced in South Germany. The method is very simple ; selected logs are held against a wet millstone until they are ground to powder. The pulp that is obtained in this way has not, of course, exactly a fibrous structure ; its readiness to be felted is very small. And besides this, it is full of resins from the trees from which it has been made, and this makes the bleaching of it very

difficult if not impossible. This wood pulp can only be worked up with rags, the longer fibres of which give the needful tenacity to the paper, while the wood pulp increases the weight. This substance is indeed rather a "loading" than a substitute for rags.

The employment of such loading stuffs has been carried much further. Gypsum, and substances of like nature, are mixed with the paper pulp; such substances cannot, it is true, improve the felting of the pulp, but when they are deposited between the felted fibres of the paper they add to the weight, although at the same time they reduce the strength, of the paper.

Besides the purely mechanical process of grinding wood, a method was introduced, almost at the same time, into the paper industry for disintegrating straw by boiling it with soda lye, and so obtaining a product which, after thorough washing with water, could be at once reduced to pulp in a "breaker." The pulp that is thus obtained can be bleached by chloride of lime, and it may then be mixed freely with the genuine cellulose that is used in the paper factory. A pulp is obtained by a similar method from esparto grass.

While the disintegration, by boiling, of straw or esparto grass, and like substances, is easily carried out, the performance of the same process with wood is much more difficult, because we are dealing with a vastly more solid material. The process at first adopted as the most convenient was what is known as the soda cellulose treatment. This process, introduced by an American named Watt in 1860, consisted in boiling wood, chiefly fir and pine wood, with soda lye under a greatly increased pressure. The vessels were placed, like steam boilers, directly over the fire. The raw material was cut in thin shavings perpendicularly to

the stem, and these were placed, in wire supports, in the vessels into which the lye was then run. The pressure must be raised to about ten atmospheres, in order to effect the complete breaking up of the wood. When the boiling was finished the wood shavings appeared dark brown. As all the substances that incrust and hold together the cellulose in the wood had by this time become soluble in water, these substances were dissolved and removed by stamping the shavings in large quantities of water, in a suitable apparatus: and, after washing, only the cellulose remained. The product, called *soda cellulose*, came into the market with fairly long fibres, and as it was easily bleached it was used for working up with other materials into paper.

The substance known as *sulphite cellulose* has been a keen competitor against the soda cellulose since the year 1884, and has gradually superseded it. Since 1905 soda cellulose has almost ceased to be used.

It is of course perfectly conceivable that there should be other substances besides soda lye capable of disintegrating the bodies that incrust the cellulose in woods, without exerting too much action on the cellulose itself. Many such substances have been discovered in the course of time, but the only one that has been found technically useful is *acid sulphite of lime.* The name sulphite cellulose is given because the reagent used in the process is a sulphite—that is, a salt of sulphurous acid.

The process of making sulphite cellulose was made technically practicable by Mitscherlich; although experiments in the same direction had been made before him by others, yet these experiments led to no results. There is indeed an English patent dating from 1866 wherein the whole process is nearly described, but only nearly, for never did a pound of cellulose made by that patent come into the market,

Nothing can be included in a German patent that has been described by any one, anywhere, in the same or in a very similar manner, until after fifty years have elapsed since the last publication. The conditions are therefore very unfavourable to the discoverer. We know from what we learnt about tanning that almost all woods contain tanning bodies; these substances must go into solution, along with the other non-cellulose constituents of the wood, when wood is disintegrated to cellulose by boiling. Hence these substances must be found at last in the aqueous liquid, provided they are not decomposed by the special process of boiling that may have been used. The specification of the patent therefore stated that a liquor could be obtained by boiling wood with acid sulphite of lime, which liquor was serviceable for tanning purposes, while cellulose was obtained as a bye-product.

But now, what is acid sulphite of lime?

We all know that when sulphur is ignited it burns with a very penetrating odour, and gradually disappears, and just as carbon produces the gas carbonic acid when it burns, so burning sulphur forms sulphurous acid, which is also a gas. Acids combine with bases to form salts (see p. 49); if, then, the gas coming from a furnace in which sulphur is burning is led into a chimney that is not empty as chimneys usually are but is filled with limestone which is kept moist, the sulphurous acid will not escape into the air, but will combine with the basic lime to form sulphite of lime. As there will be much sulphurous acid gas at the bottom of the chimney, and as this gas is very soluble in water, an acid solution of the gas will be produced at this point, and the sulphite of lime that is formed will dissolve in this acid liquor to form acid sulphite of lime.

A solution of acid sulphite of lime attacks most metals energetically. Lead is the metal which best withstands the action of chemical reagents, and at the same time is not too costly when it has to be used in considerable quantities; for this reason leaden vessels, or vessels covered with lead, are very often used in chemical industries.

If cellulose is to be prepared from wood by the action of the acid sulphite liquor, the wood must be boiled with the liquor under a pressure of about three atmospheres. Now lead is so soft that it is impossible to make leaden vessels that will withstand much pressure; hence it was a very difficult problem to construct vessels suitable for carrying out the process of making sulphite cellulose on the large scale. The following method is now employed. An ordinary boiler is lined inside with resin on which are laid plates of lead; these plates are then covered with acid-resisting flagstones arranged in two layers in such a way that the joints between the upper and the under layers are separated from one another by half the breadth of one of the stones. Several systems of leaden pipes are placed in the boiler for the purpose of heating it, and steam is led in through these pipes from another boiler. It is necessary to have several sets of pipes, because one or other of the pipes occasionally bursts.

Wood which has been boiled with the acid sulphite of lime liquor leaves the boilers less coloured than when it went in; in this respect it differs from wood boiled with soda lye. Remembering that sulphurous acid is an effectual bleaching agent (see p. 147) we see that there can be no difficulty in turning out perfectly white cellulose by this process.

The best product is obtained from the wood of the silver fir. This tree does not flourish farther north than the Main; and as the trees are most suited for cellulose making when

they are about fifteen years old, and the demand has greatly increased of late years, the planting of these trees is a matter to be commended to the consideration of the managers of forestry. Farther north much use is made of pinewood.

The fact that a medium-sized establishment for making sulphite cellulose consumes daily five or six acres of well-timbered pine-forest, gives us a good notion of the scale on which the manufacture of this substance is now carried on.

Sulphite cellulose has almost driven out soda cellulose. Not only this, but sulphite cellulose is taking the place of the raw material that was formerly employed in paper making. We have already learned (see p. 111) that spirits can be made from the liquor obtained in preparing sulphite cellulose.

Finally it should be mentioned, as showing the superiority of the cellulose made by the sulphite process, that some very skilful workers have made attempts so to disintegrate wood by this process that cellulose may be obtained in such long fibres that it may be interwoven with cotton and thus serve as a partial substitute for that material.

These attempts, which have been in progress since 1890, have not led directly to the desired result; but fibres which can be woven have been obtained in the following way. Paper made from cellulose is run over ribbed cylinders, so that slips, instead of sheets, of paper are produced, and these are converted, while moist, into threads, by twisting, which is a kind of spinning. These paper-threads are then used as the woof, and threads of cotton as the warp, in weaving a fabric, 70 per cent. of which consists of paper. The fabric has been called *silvalin* (from the Latin *silva*, a wood, or forest). The durability of silvalin is remarkable; sacks made of it, and filled with goods, have gone round the world

and been none the worse. It seems as if silvalin yarn would become a not inconsiderable rival of jute.

When one considers that materials made from wood by chemical processes are constantly finding new applications, one cannot be astonished at the great rise in the price of wood.

LECTURE IX

Burnt lime—Potash—Soda by Leblanc's process—Sulphuric acid—Sulphate of Soda—Nitric acid—Bleaching powder—Soda crystals—Ammonia soda process—Ashes of molasses—Ashes from the washings of wool—Soap—Caustic alkali—Caustic soda—Soft soaps—Loaded soaps—Curd soaps—Hard and soft waters—Plasters.

THE preparation of *soaps*, which we have now to consider, is brought about by the action of *caustic alkalis* on fats. Before we are in a position to deal with soaps we must consider in some detail the caustic alkalis, and also the carbonated alkalis, as the manufacture of one of these cannot be separated from that of the other.

The burning, or, to speak more accurately, the intense heating, of limestone was practised in ancient times; and in these days burnt lime was the only caustic alkali known throughout the world.

The following considerations explain why burnt lime has been known since ancient times. When stones are placed so as to form a hearth wherein a fire is to be burned, most of the stones used for this purpose remain unchanged when the fire has gone out. Only one kind of stone is altogether altered by the process. When that stone has become cold, the falling of rain on it, or the pouring of water upon it, causes it to become hot again; the water begins to pass off as steam, and the hard stone falls to powder. The stone which

behaves thus is found abundantly in nature. It is called limestone; the purest forms of it are called marble, calcspar, or chalk. Burnt limestone, or burnt lime as it is generally called, is used for making mortar, to which we shall refer hereafter. With the help of what we have already learned, we are able to explain the behaviour of this stone, in the following way. Limestone is carbonate of lime. When it is heated, carbonic acid escapes as a gas, and lime * remains. Natural limestone is an excellent building material, because it is but slightly affected by weather-conditions. Burnt limestone, however, falls to pieces, *slakes* as it is said, by the action of water. By reason of the chemical reaction between burnt lime and water, so much heat is produced that some of the water is changed to steam.

Slaked lime has very caustic, that is, destructive, properties; hence, it is known as caustic lime. Inasmuch as it combines with acids to form salts, it is chemically a base or an alkali (p. 49).

Although lime slakes with water, and combines with some of the water, nevertheless it is but slightly soluble in water. Combination with water, and dissolving in water, are two quite different things. Already in the Middle Ages, the soap-maker knew how to use lime for making an alkali which is very soluble in water. This substance was known as *caustic alkali.* It is made to-day, as it was made in ancient times, from potashes, by using caustic lime.

We shall consider the process for making caustic alkali after we have made clear what potashes is (see p. 178).

* Lime is the oxide of a metal, *calcium*; calcium oxide eagerly combines with water. In this combination, much heat is produced; the calcium oxide changes to calcium hydroxide, which is known as *slaked lime.*

$$CaO + H_2O = Ca(OH)_2.$$
Calcium oxide + Water = Calcium hydroxide.

We know (see p. 37) that all land plants must have potash salts if they are to live; every kind of wood, for instance, contains potash salts, and when the wood is burnt these salts are found in the ashes. The ashes of plants contain potash salts chiefly as *carbonate of potash*, which is a salt that is very soluble in water. If the ashes are boiled with water in pots the potash salts go into solution, and when this solution is evaporated these salts are found in the solid residue, which is known as potashes (or pot-ashes).

Potashes is a substance that was, and is, very much used; it is employed, for instance, in making soap, in manufacturing glass, in dyeing, etc. As forests were cut down the supply of potashes became less; this narrowing of the supply made itself definitely felt at first in France, where, as long ago as 1775, the Academy of Paris offered a prize of 2,500 *livres* (about £5,000), not for a process for making potashes artificially, but for a method whereby common salt could be converted into soda, because soda could be used, in most cases, as a substitute for potash.

Matters were in this position. Potashes is carbonate of potash; soda was also known to be a carbonate. No natural source of potash was known other than potashes. The Stassfurt salt deposits (see p. 46) were not discovered till the second half of the nineteenth century; and there was no method known at that time for making potash from other compounds of potash.

The only source of soda salts available at that time was the ash of sea plants, which plants contain soda (obtained by them from the salt in the sea) in place of the potash of land plants; this ash was prepared chiefly in North Spain, and was known as *barilla*. The greater part of the *barilla* of that time consisted of impurities; only about 5 per cent. of soda was present in it. Nevertheless so great was the de-

mand, or we might say the greediness, for soda that this *barilla* was used in various industries. Now soda is *carbonate of sodium*, and it was known even in those days that there is a practically unlimited supply of sodium compounds in *common salt*, which is composed of sodium and chlorine. And it so was that a prize was offered, in 1775, for a method of making soda from salt, because there seemed to be no possibility of finding a process for manufacturing potash salts.

The following figures give a notion of the value of soda salts. In 1814 a ton of soda crystals cost about £65 ; in 1824 the cost was about £32 ; and it is now about £3. The prices that ruled at the time we are speaking of made possible a very large profit on the manufacture of soda.

After many unsuccessful attempts by other people, the problem was solved by Leblanc, who took out a patent in 1791.

Leblanc's method was extremely complicated. To conduct the process at all requires chemical knowledge of the most varied kind ; and to apply the improvements that have been worked out in the laboratory, and to carry into practice the many subsidiary manufactures that have sprung from this main industry, demand so much technical ability that it may be said that this manufacture is not merely the foundation of the immense chemical industries of the present day, but it is also the guiding spirit in these industries. The fame of the Leblanc process will remain for all time.

Leblanc did not, any more than his contemporaries, make it possible to change common salt—that is, chloride of sodium —directly into carbonate of soda. His discovery consisted in making it possible to change sulphate of soda—which is

obtained from common salt without much difficulty—into carbonate of soda.

Leblanc's process consists of the following parts. Common salt (chloride of sodium) is changed into *sulphate of soda* by heating with sulphuric acid. The sulphate of soda is then mixed with coal and chalk (chalk is carbonate of lime), and the mixture is heated until it melts ; the melted mass is lixiviated with water, and the solution which contains carbonate of soda is evaporated ; the crystals that separate are the *soda crystals* of commerce.

The salt sulphate of soda, into which common salt is converted in the first stage of the manufacture of soda, is ordinarily known as *Glauber's salt*, from Glauber, who first prepared it in 1645.

The manufacture of soda by the Leblanc process requires the use of *sulphuric acid* ; and the manufacture of this acid is intimately bound up with that of soda by Leblanc's method.

We know that gaseous sulphurous acid is produced when sulphur is burnt (see p. 172). Now to convert sulphurous into sulphuric acid an atom of oxygen must be added to the former. This can scarcely be done directly ; but the addition of the oxygen is performed easily in presence of *nitric acid.* Experience has shown that the process is best conducted in large chambers, which are made of lead that they may resist the action of the acid (cf. p. 173). The nitric acid loses oxygen which goes to oxidise the sulphurous acid to sulphuric acid. As constant supplies of air and water vapour are led into the chamber, the products of the deoxidation of the nitric acid are constantly changed back into nitric acid ; the nitric acid thus serves as a carrier of the oxygen of the air to the sulphurous acid, and hence a comparatively small quantity

of nitric acid is required. The sulphuric acid collects as a liquid on the bottom of the chamber.

The manufacture of sulphuric acid evidently carries with it the making of nitric acid. That acid is sometimes called [*aqua fortis*, and sometimes] *parting acid*, because it is used to part gold and silver, only the latter of these metals being soluble in nitric acid. The acid is made by the action of sulphuric acid on saltpetre, and soda saltpetre is used because of its cheapness (cf. Chili saltpetre on p. 50). The products of the reaction of these two compounds are sulphate of soda, and nitric acid which is easily separated by distillation.

After about 100 years, during which the manufacture of sulphuric acid by the agency of nitric acid had been more and more improved, a serious competitor appeared about the year 1896 in the form of a new method of making the acid. This method is as follows. Very finely divided platinum has the property of causing many chemical reactions to proceed which do not occur in the absence of it. This behaviour of finely divided platinum reminds one slightly of that of pepsin (see p. 53) or of diastase (see p. 100). Sulphuric acid is produced by bringing sulphurous acid and air—of course, it is only the oxygen of the air that is concerned in the process—into contact with finely divided platinum. This reaction, which seems so simple and has been known in the laboratory for a long time, is so difficult to carry out on the large scale that it is only recently that all difficulties have been overcome.

Sulphuric acid used to be prepared in the manner indicated above from sulphur; but in the year 1838 the price of sulphur rose from £5 10*s*. to £15 per ton, because in that year the then King of Naples leased to a Marseilles firm a monopoly for making sulphur in Sicily, which is the only European country where sulphur is found in quantity. The making of

sulphur began in earnest in Louisiana (America) only in 1906. The English sulphuric acid factories—and almost all the factories at that time were in England—grumbled exceedingly, and a kind of sulphur war threatened to break out; the result was that the monopoly was withdrawn.

But meanwhile necessity had led to new inventions. It is true that there is not much free sulphur to be found in Europe; but there are numerous deposits of sulphur compounds scattered about the world, especially deposits of sulphide of iron which forms the mineral known as *pyrites*. Pyrites can be burnt in ovens; and under these conditions the sulphur of the pyrites—and pyrites contains about 48 per cent. of sulphur—is burnt to sulphurous acid, while the iron is burnt to oxide of iron which can be used in iron making. There is also the mineral *copper pyrites*, coming for the most part from Spain, which can be used for making sulphuric acid; this mineral is willingly employed by the sulphuric acid maker, because the extraction of copper from the burnt residue is a paying business. Here is an example of a subsidiary industry depending on the Leblanc soda industry.

Sulphuric acid is one of those commercial articles which are manufactured in enormous quantities. Besides what is required in soda making, we have but to think what quantities of sulphuric acid must be used every year in the process of decomposing phosphorite and burnt bones to make them into artificial manures, and how much must be needed for manufacturing sulphate of ammonia for the use of the farmers (cf. pp. 43 and 50).

The quantity of sulphuric acid manufactured in the world in the year 1909 amounted to about 8,000,000 tons. Of this quantity, England made about 2,100,000 tons, Germany about 1,385,000 tons, the United States about 1,300,000 tons, and France about 800,000 tons. In that year, about 240

tons of sulphuric acid were made each hour in England ; the price of a ton of the acid was about £3 10*s*.

When sulphuric acid reacts with common salt (chloride of sodium) not only is sulphate of sodium formed, but hydrochloric acid is also produced.

Common salt + sulphuric acid = sulphate of soda + hydrochloric acid.

Hydrochloric acid is a gas, and like sulphurous acid or ammonia gas it is very soluble in water. Commercial hydrochloric acid, which is an aqueous solution of the gas, contains about 33 per cent. of the acid. This commercial acid is a liquid which fumes slightly in the air ; when it is evaporated the hydrochloric acid gas that is given off forms clouds with the moisture of the air. In the earlier days of the soda industry no use could be found for the hydrochloric acid produced in the manufacture, and, as it was allowed to escape into the air with the gases from the furnaces, it formed a terrible nuisance. All vegetation died in the neighbourhood of the soda factories, and complaints were loud and deep. In a suburb of Brussels the tools of the artisans living there were so corroded by the acid as to become useless in a short time. An attempt was made in one factory to get rid of the gas by leading it up a chimney 150 metres [nearly 500 feet] high—that is, about twice the height of an ordinary church spire—but instead of mixing with the air at the top of the chimney, the gas fell, in wet weather, in heavy clouds on to the ground beneath.

To stop the complaints some English factories were put out of the way on to small islands in the canals; but although the great solubility of hydrochloric acid in water was well known, there was no possibility of getting rid of the acid by

this procedure, for the aqueous hydrochloric acid could not be run into rivers, as it would kill the fish.

Hydrochloric acid remained for long a veritable plague to the manufacturers; but gradually matters completely changed. Hydrochloric acid found its most important use in making chloride of lime, which was consumed in large quantities for bleaching (see p. 145).

In order to make chloride of lime from hydrochloric acid the gaseous acid is first of all led into water. The destructive action of the acid gas on the surroundings of the works is thus obviated. The aqueous solution of the acid is then heated with *pyrolusite*, a mineral which consists chiefly of peroxide of manganese; in this reaction between manganese peroxide, which is very rich in oxygen, and hydrochloric acid, which is a compound of hydrogen and chlorine, the oxygen of the manganese peroxide combines with the hydrogen of the acid to form water, and chlorine is set free; it is then only necessary to lead the chlorine into chambers wherein lime is spread in order to form chloride of lime.

Manganese peroxide + hydrochloric acid = manganese chloride + water + chlorine gas.

A very considerable amount of hydrochloric acid is purchased by those who conduct other chemical industries for use in their works.

For starting the first manufactory for carrying out his process Leblanc naturally required a large sum of money. The money was furnished by the Duke of Orleans, afterwards known as Philippe Égalité, on the strength of a report testifying to the soundness of the project by d'Arcet, professor of chemistry in the *Collège de France*, at Paris.

Égalité's life was brought to an end in 1793 by the guillotine,

and the soda factory was confiscated along with his other possessions. After this the constant wars of the Republic, by preventing the transport of goods to the sea, caused potashes to become very scarce in France, and a decree was issued by *The Committee of Public Safety*, commanding that all the processes for making soda that had been discovered (see pp. 178, 179) should be made known. In this way Leblanc's patent collapsed. The factory was restored to Leblanc in 1799; but he could not carry it on for want of means, and in 1806 this great inventor committed suicide in despair.

The process of Leblanc was not forgotten, but it dragged along without much effect until it was taken up and developed by some English manufacturers. The soda industry did not grow much, however, in England until after 1824, in which year the duty of about £30 per ton was removed.

The soda manufactured in London must for a time have been given away, in order to accustom the soap-makers to the use of soda and to induce them to give up the employment of *barilla* (see p. 178). But this state of affairs was soon changed, as it was found that the work of soap-making was done much more quickly and conveniently by using the pure soda than when the unsatisfactory barilla was employed. Indeed after a time people were glad to get hold of the crude melted masses that came from the soda ovens, and to lixiviate these for themselves, rather than to use barilla. Soda had gained a firm footing. The manufacture of soda by Leblanc's process began in Germany in 1830 at Schönebeck on the Elbe.

To make soda by the Leblanc process it is necessary to melt together Glauber's salt (sulphate of soda), chalk, and

coal. The sodium that goes to make the soda is obtained from the Glauber's salt, and the carbonic acid from the chalk, which, as we know, is carbonate of lime. The reactions that occur in the process of melting are so complicated that it is not possible for us to go into them in this place. The soda (carbonate of sodium) in the melted product is dissolved out by lixiviating with water, and this solution is evaporated until less water remains than suffices to keep the soda in solution; the soda crystallises out from this liquid as it cools. The soda crystals that form contain almost exactly 63 per cent. of water, which is held fast by the crystals and is known as *water of crystallisation.* Many salts have this property of binding to themselves definite quantities of water of crystallisation.

When soda crystals are exposed to the air for a long time they undergo a visible change—they lose a part of their water of crystallisation, and the crystals fall to powder, as it is only when combined with the water of crystallisation that they exhibit their characteristic crystalline form. The large amount of water of crystallisation in soda crystals would add unnecessarily to the cost of carriage, and for this reason it is customary to manufacture anhydrous carbonate of soda by strongly heating soda crystals until all the water of crystallisation is removed. The product known as *calcined soda* is sent into the market in the form of a white powder.

We have now become acquainted with the broad outlines of the Leblanc soda process, and we have also learnt something of the chief of those bye-industries which have been created by this process. The existence of this process, which had been carried on successfully for something like sixty years, began to be threatened about the beginning of the year 1880; and the making of soda by the Leblanc method

has now virtually ceased. How that has come about is now to be described.

A much simpler method for transforming common salt into soda than that used in the Leblanc process has been known for a long time. The principle of this method, which can easily be carried out in the laboratory, is as follows. The base ammonia combines with a certain quantity of carbonic acid to produce carbonate of ammonium, and it also combines with twice as much carbonic acid to form bicarbonate of ammonium; when a solution of the last-named salt is added to a solution of common salt double decomposition occurs, and a precipitate of the comparatively insoluble bicarbonate of soda is produced, while salammoniac (chloride of ammonium) remains in solution.

Bicarbonate of ammonium (soluble in water) + sodium chloride (soluble in water) =

bicarbonate of soda (only slightly soluble in water, therefore precipitates) + chloride of ammonium (soluble in water; remains in solution).

By this reaction common salt is changed directly into bicarbonate of soda.

The process based on this reaction is theoretically extremely simple. The first patent dates from 1838; and we know that soda was made by this process in the years 1854–57 in a French factory, and was sent into the market under the name *ammonia soda*. But as the ammonia process was given up after a time because it could not compete with the Leblanc process, there must have been difficulties in the way of carrying out the reactions on a manufacturing scale. These difficulties, which are chiefly mechanical, and are due to the stoppage of the pipes by salts that separate during the process, were finally overcome by Solvay. Almost the whole of the world's gigantic demand for soda is now satisfied by the use of the Solvay process.

The process is carried out somewhat as follows. Ammonia gas is pumped into a solution of common salt, in a closed apparatus, and when sufficient ammonia is present carbonic acid gas is then forced into the solution. Bicarbonate of ammonium is thus formed in the liquid, and by reacting with the sodium chloride, this salt produces bicarbonate of soda which separates as a solid.

The common salt required for the process is got from the salt mines, or salt brine is pumped directly from the salt-bearing strata, and the ammonia that is needed comes from the gas works. The large quantities of carbonic acid that the process demands are obtained by calcining chalk in ovens, and the gas that is given off is forced by air-pumps into the brine.

When chalk is calcined in lime kilns it separates into lime and carbonic acid gas; as carbonic acid is also produced by the burning of the carbonaceous fuel used for heating the kilns, the gases given off from these kilns are very rich in carbonic acid, and they are used in many industries, besides soda making, wherein that gas is required.

The bicarbonate of soda obtained in the way described has to be transformed into "*soda*," which is the normal carbonate. To do this it is only necessary to calcine the bicarbonate at a moderate temperature, whereby the second molecule of carbonic acid is driven off.

The liquids drawn off from the bicarbonate of soda contain salammoniac; and as a matter of course ammonia is recovered from these liquids. Ammonia is driven out from its combinations by any base that is stronger than itself; when, therefore, these solutions are boiled with caustic lime, which is produced in the lime kilns of the soda factory along with carbonic acid, ammonia is driven out by the more basic lime. The ammonia obtained in this way is pumped

into a fresh lot of brine, and the manufacture goes on uninterruptedly.

The final bye-product of the manufacture is the chloride of calcium produced by boiling the solutions of salammoniac with lime.

Chloride of ammonium + lime = chloride of calcium + ammonia.

This solution, or the solid chloride of calcium produced by evaporating this solution, has not yet found any special application, and there is nothing to be done with the large quantities of this substance that accumulate in the ammonia soda works except to run them into the nearest river.

It is evident that the chlorine which is originally brought into the process in the form of chloride of sodium is not used in the Solvay process, but is thrown away as chloride of calcium. In the Leblanc process, on the other hand, the chlorine of the common salt is recovered as hydrochloric acid, which, either as it is or when transformed into bleaching powder, etc., has a considerable value.

Only the initial stage of the Leblanc process has remained. There are factories where common salt is heated with sulphuric acid, to obtain hydrochloric acid. But these factories do not work up the sulphate of soda which they obtain into soda; they sell it for glass-making (see Lecture X.). Nor do they make chlorine from their hydrochloric acid, but seek to sell it to other industries which use that acid. The reason for this is as follows. The electric current (of the action of which we shall learn something in Lecture XI.) is able to decompose many substances into the elements of which they are composed. Chlorine can be obtained by decomposing chloride of sodium (common salt), or chloride of potassium—plentifully supplied by the Stassfurt deposits (see p. 46)—by the electric current; and electricity is now to be had at a cheap rate.

The other products of the action of the current on these salts are caustic soda and caustic potash respectively. We shall find that these *alkalis* are used in making soaps ; of their use in paper making we know already.

These things do not seem to be in keeping with the dicta of moral philosophy which tell us that every worthy piece of work receives its reward. We see here that a good piece of work demolishes another equally good, and that progress is made by the new constantly replacing the old.

Although the consumption of soda is very great, and soda has driven potash out of many industries, nevertheless there is still a very considerable demand for potash. The chief source of potash salts is wood ashes, which in recent years comes in large quantities from the Caucasus. Two quite new sources of potash salts have, however, been made available since the middle of last century ; these are *molasses* and the *washings of wool.*

Molasses is the name given to the final mother-liquor in the manufacture of sugar (see p. 76). Although means are now known for extracting the sugar from molasses, yet a great deal of this substance is still used for making spirits by fermentation. The residue that is left (see p. 107) when the spirit is distilled off from beetroot molasses has no value as a food, as it contains only the salts that were originally present in the beets and went into solution when the beets were macerated with water. These salts, coming as they do from the soil, are rich in potash ; if the molasses residue is evaporated to dryness and calcined the potash salts can be obtained by then lixiviating with water.

The second source of potash salts mentioned above is more remarkable. Factories have been established for washing the crude wool that is brought in large quantities into Europe,

chiefly from Australia, Africa, and South America. The grease that is taken out of the wool by the washing accumulates in the wash water, and this grease has been found by experiment to be rich in potash salts ; these salts are obtained by evaporating the wash water to dryness, calcining, and extracting with water. Considerable quantities of potash salts are obtained from this source, and the extraction of these salts has become a paying process.

Neither carbonate of potash nor carbonate of soda is directly applicable to the making of *soap*, which is the subject we have now to consider. These compounds do not act upon the fats from which soap is manufactured. The carbonates of potash and soda must be transformed into caustic potash and caustic soda respectively. This is done in the following way, if the caustic alkali is not obtained directly by an electrolytic process, a method which has become possible in the last few years.

We know (p. 176) that limestone is decomposed, by heating, into carbonic acid and caustic lime. One might expect that carbonate of potash and carbonate of soda would be changed by heat into carbonic acid and caustic alkali ; but experiment shows that this is not practicable. These two compounds do not decompose even at very high temperatures. Unlike limestone, the carbonates of potash and soda dissolve in water. If burnt lime is added to these solutions, the lime withdraws and combines with the carbonic acid, forming carbonate of lime, and caustic potash or caustic soda. As carbonate of lime is insoluble in water, it sinks, and the supernatant liquid can be drawn off. The following equations show what occurs :

Carbonate of potash + caustic lime = caustic potash + carbonate of lime.

Carbonate of soda + caustic lime = caustic soda + carbonate of lime.

The caustic lye of the soap maker can thus be prepared. When this lye is boiled with fats, which, as we know, are compounds of glycerin with fatty acids (see p. 19), the decomposition represented in the following scheme occurs:

Compounds of glycerin and fatty acids + alkali = compounds of alkali and fatty acids + glycerin.

Soap is a mixture of compounds of fatty acids with alkali.

We are told by the elder Pliny that the Germans prepared an ointment by boiling ashes with fat; but it was not until about the second century A.D. that this substance began to be used for cleansing purposes, although at that time and for some time afterwards it continued to be employed more as a medicament than a detergent. We know that Marseilles boasted a flourishing soap industry about the year 1000, and that it was not till the fifteenth century that the Venetian factories entered into competition with Marseilles; from that time the art of soap making spread gradually over the world.

The manufacture of soap remained a purely empirical handicraft, as nothing was known of the chemical changes involved in the processes, until, in the early years of the nineteenth century, the French chemist Chevreul made known the nature of the fats, showing them to be compounds of glycerin with fatty acids. This discovery threw light on the processes of soap making; and when, in addition to this, the soap maker was able to use the comparatively cheap caustic soda as well as the more expensive potash, the manufacture of soap began to expand, and this went on until to-day soap has been brought within the reach of even the poorest person.

The fact that the only fats at the disposal of the soap maker were animal tallow and olive oil gave a certain stability

to the soap industry in older times; but the extension of commerce is now constantly bringing new kinds of fat and new oils into the soap factories, and these require special methods of treatment, and demand much consideration on the part of the manufacturer if he is to retain his position in competition with his ever-active neighbours.

Every one knows the statement, All misfortunes come from change. This saying comes to our minds in the present instance. But it would be better to say, Every advance comes from change. For we certainly do not share the opinion that it would be a fortunate thing for us to stand still in the old ways of the centuries that are past.

Fat is nowadays a bye-product of many industries; this is true, for instance, of the fat from bones. We have already spoken in some detail of the ways in which bones are most advantageously made use of (see p. 44). The fat of bones is of no value for the purposes we have spoken of, and it is therefore removed before the bones are used. It used to be the custom to boil the bones vigorously with water; the fat was then separated and rose to the surface of the water. But this method did not completely remove the fat.

The method now in use consists in breaking up the bones into suitable pieces, and then extracting with petroleum ether in special apparatus; the whole of the fat is obtained in solution by this process.

The chief difference between soaps made by the use of potash and those made by using soda is that the former are soft soaps while the latter are hard soaps.

The process for making soft soap consists in boiling the cheapest kinds of soluble oils, such as fish oil, hemp oil, or linseed oil (and, since 1910, oil made from the seeds of the soy plant), with potash lye in iron vessels. If the lye is

allowed to act slowly the soap may be taken to be ready when the contents of the vessels have acquired a pasty consistency. Soap made in this way does not dry in the air, but always remains soft. It can bear a good deal of loading —that is, substances may be added to it pretty freely without their presence being shown. For instance, it can take up a considerable quantity of *water glass* (that is, *silicate of soda*, to be spoken of later under glass); and solutions of sulphate of potash and other substances are also employed. Such additions are useless so far as the detergent power of the soap is concerned, but they serve to increase the weight of the soap, and as these loading substances are cheaper than soft soap it is possible to sell loaded soap at an extremely low price.

Until a method for making soda was worked out, in the way already described, the only alkali available for making soap was caustic potash got from potashes, and therefore soft soap was the only soap that could be manufactured directly. But the discovery was made at an early stage of the manufacture that the addition of common salt after boiling the fat with caustic potash produced a marked change in the product. The effect of salting is to cause the separation of a liquid which lies beneath the soap and can be drained off, and also to make the soap carry with it much less water and to cause it to separate as a white semi-solid mass which becomes hard when it is cold.

The cause of this change is found in the reaction which takes place between the common salt (chloride of sodium) and the potash salts of the fatty acids, resulting in the production of chloride of potassium and soda salts of the fatty acids.

Potash salts of fatty acids + Chloride of sodium = Soda salts of fatty acids +
Chloride of potassium.

Soft soap. Common salt. Hard soap.

The fatty salts of soda are not able to combine with all the water which comes from the lye; some of this water therefore separates as a liquid underlayer, and this layer also contains in itself the glycerin that has been separated from the fats by the process of saponification, and the chloride of potassium; these two are thus removed in the watery layer. If one salting is not sufficient the process is repeated. The genuine toilet soaps are formed by the solidification of the fatty salts separated by this process. As the salting is never completely effective, these toilet soaps always contain some of the fatty salts of potash, that is some non-solidifying soap, and it is this which gives them their pleasant softness. One hundred parts of tallow treated in the way described yield about 160 parts of good soap containing from 10 to 20 per cent. of water.

But the greater part of the soda soaps made at present are made by boiling fats with caustic soda—that is to say, by a process which yields hard soaps directly.

Hard soaps can be loaded as well as soft soaps. If the product of saponification is boiled with water for a long time, and is then let cool, the soap solidifies to a hard mass without the separation of a watery under-layer. Such soap contains about 50 per cent. of water; it is known as *fitted soap*.

High-class loaded soda soaps are best prepared with the help of cocoanut oil. The white pulp of the fruit of the cocoa palm, which grows in tropical countries, is dried and exported to Europe, where a fat is extracted amounting to about 68 per cent. of the weight of the substance. This fat melts at about 21° C. [about 70° F.]; it is therefore fairly solid at ordinary temperatures, and because of its consistency is known as cocoanut butter.

Attempts have been made to prepare a substitute for butter from this substance by removing the more volatile

ingredients by passing superheated steam into the liquefied oil, stirring the oil at the same time with soda solution whereby the free fatty acids are neutralised, drawing off the melted oil and letting it solidify. A butter-like substance quite free from rancid taste is thus obtained which is harmless, and serves as the starting point for making a substitute for butter (see p. 65).

Soap is not made from cocoanut oil alone, because of the very disagreeable odour which always persists in this oil, but from a mixture of one part of this oil and two parts of palm oil and a little tallow.

The palm oil is derived from the oil-yielding palms that flourish on the west coast of Africa and in Central America. The flesh of the fruit and the seeds of these palms are rich in oil. The fruit is boiled by the natives to obtain the oil, and the seeds, which are very hard, are sent to Europe, where they are pressed. These seeds yield about 40 per cent. of their weight of palm fat, and the residue serves as an excellent oil-cake fodder, especially for milk cows (see p. 60).

Cocoanut oil is very easily saponified, and this readiness to undergo saponification belongs also to mixtures which contain this oil. Complete saponification is accomplished by heating to about 40° C. [about 105° F.], which is much under the boiling-point, with concentrated caustic soda lye containing a little carbonate of soda; the whole liquid solidifies on cooling, and the soap is made. Inasmuch as all the water of the lye is enclosed in the soap, as much as from 300 to 600 parts of soap are obtained from 100 parts of the mixture of oils—that is to say, nearly twice the yield that is got from tallow.

Resin soaps are often spoken of nowadays. A good soap, serviceable for ordinary requirements, cannot be made from resins alone—*colophony* is the resin chiefly used—but we have already seen that soap solutions made by boiling resins with

soda lye are used for sizing paper (see p. 166). But if soap is being made from tallow or palm oil, and a quantity of resin equal to about half the amount of the fat that would normally be employed is added, in place of fat, to the boiling soap paste, this resin is saponified along with the fat, and a very cheap and very useful resin-fat soap is obtained.

Genuine soaps then are prepared by boiling tallow or other similar fat, or oils, with caustic soda or caustic potash lye. Now we know that there are many other alkalis besides soda and potash, hence there must be other compounds of fatty acids and alkalis besides those that are known as hard soap and soft soap.

The strongest alkali, in the chemical meaning of the term, is burnt lime. Now the compound of lime with the fatty acids that is indicated by theory has been actually prepared. But this compound is insoluble in water ; when it is mixed with water it sinks to the bottom as any other insoluble powder would do, and the water does not froth when shaken up, nor has it any of the other properties that belong to a solution of soap. This substance is indeed exceedingly inconvenient in everyday life. Because of its insolubility in water it precipitates whenever an opportunity is given for its formation ; if we bring soda soap or potash soap into ordinary water this compound of lime with the fatty acids of the soap is produced. It is well known that all kinds of waters, except distilled water, contain more or less chalk ; hence whenever soap is brought into ordinary water used for domestic purposes this lime compound is formed, and so much of the fatty acids of the soap as enters into combination with lime ceases to be available for washing purposes. The more chalk a water contains the more of this lime compound is formed, and therefore the greater is the destruction of soap. For it is only after all the lime has been combined with the fatty acids

of the soap that the water can have the properties of a solution of soap and can exert those detergent effects for which we use soap and water.

It is customary, then, in daily life, to distinguish between *soft waters* and *hard waters*. The soft waters, such as river water, are poor in chalk, and only a little soap is needed to make these waters lather; but hard waters, such as spring water, contain much chalk, and they consume a considerable quantity of soap, reacting with it to form lime salts of the fatty acids of the soap, before a lather begins to be produced.

The compounds of lime with the fatty acids that are contained in soaps cannot be used for washing purposes; but the state of affairs is different when oxide of lead is used as an alkali and fats are boiled with this substance. A compound of lead with the fatty acid is formed—that is to say, a lead soap is produced; and this compound is of the nature of a *plaster*. Plasters are substances more tenacious and harder than ointments, and they are used, just as ointments are used, as healing agents for external application. Pure lead soaps are used as plasters, and also lead soaps modified by additions of very different sorts of materials. The German sticking plaster, for instance, is a mixture, spread on linen, of 500 parts lead soap, to which, heated to 60° or 80° C. [about 140° to 175° F.], 50 parts of wax are added, and also 50 parts of a mixture of melted dammar resin and colophony, and 5 parts of turpentine. The English sticking plaster is an altogether different preparation. It is made by stretching strips of woven silk cloth on a frame, and brushing over these a solution of the very best glue in dilute spirit until a piece adheres firmly to the hand, after being moistened. The preparation is slightly perfumed with a little gum benzoin, or a similar substance.

LECTURE X

Glass—Glass mirrors—Potash and soda glass—Quartz glass—*Strass*—Artificial precious stones—Ruby glass—Milk glass—Clay—Bricks—Mortars—Lime sandstone bricks—Cements—Glazing—Pottery—Stoneware—Majolica ware—Porcelain—Photography—Lunar caustic—Chloride, bromide, and iodide of silver—Daguerreotypes—Development of the negative—Talbotypes—Albumen methods—Wet collodion processes—Dry silver bromide emulsion plates—Platinotypes—Photography of the spectrum—Red light—Orthochromatic plates—Colour photography—Chromegelatin—Pigment printing—Röntgen rays—Radio-activity—Radium.

IN speaking of the manufacture of soap, mention was made of silicate of soda, or water glass, which is a very soluble salt that is used for loading soft soaps. This salt and silicate of potash are the only compounds of silicic acid that are soluble in water. But these salts also become insoluble in water when they are mixed with other silicates and the mixtures are melted. For instance, if silicic acid, potash, and lime are fused together the product contains silicate of potash and silicate of lime, and is insoluble in water. This product is called *glass* when it has been prepared with proper skill and has been brought into such a form as makes it useful to us.

In making glass the practice has long been to melt together silicic acid, potashes (that is, carbonate of potash), and carbonate of lime; the carbonic acid, which is driven out from the melted compounds by the silicic acid, escapes as gas,

and there remains a mixture of silicate of potash and silicate of lime.

Silicic acid + carbonate of potash = silicate of potash + carbonic acid.
Silicic acid + carbonate of lime = silicate of lime + carbonic acid.

The salts of silicic acid are called *silicates* in chemical nomenclature; and glass may be described as a mixture of several silicates [or salts allied to silicates] melted together. This description may be applied in a very general way; it is not necessary to keep to silicic acid, potash, and carbonate of lime; as a matter of fact, in glass making sometimes one and sometimes another of these constituents is replaced wholly or in part by another acid or by other bases which experience has proved to be suitable for the objects of the manufacture. We shall have to speak of the most important of these materials.

A very high temperature is required for melting the materials that have been mentioned. This fact is sufficient of itself to relegate Pliny's story of the discovery of glass to the domain of fable. According to that story certain Phœnician merchants had made a fire under a vessel which they had supported on lumps of "*soda*";* the soda melted by the heat, and coming into contact with sand (that is, with silicic acid), and the other necessary materials on the ground, produced glass. Now such a fire as that described in Pliny's story could not have been hot enough to melt glass. At the same time we need not be astonished at finding glass objects in very ancient tombs, since we know that the art of smelting metals was practised from very early times and this art requires the maintenance of high temperatures.

* The term used by Pliny is generally translated *soda*: but it is certain that Pliny was not acquainted with the substance that we now call by this name.

Glass was exceedingly costly in the old classical days. The most famous glass factory of the Middle Ages was at Murano near Venice, and this factory, after nearly collapsing, has been revived in our own times. Glass is manufactured to-day in every country where the cost of labour is not too great.

The employment of glass in windows, for which purpose nothing can replace it, came in very gradually because of the high price of the material. Although the windows of churches had been filled with glass as early as the tenth century, yet it was not until about the fourteenth century that glass began to be used in the windows of the private houses of the rich, and several centuries passed before it had completely taken the place of the oiled paper, the stretched animal bladders, and the solid window shutters of that period. The extraordinary gladness wherewith the German singers of the early Middle Ages greeted the return of spring may have had some connection with these window coverings. Men escaped in spring from the wretchedness of spending the long days of winter in half-darkened rooms lighted by the feeble glimmer of burning pine-splinters.

Glass making then requires silicic acid. This is ready to hand either in the form of sand, which is silicic acid, or in the form of quartz, which is crystallised silicic acid. The purer the raw material the better is the result. The presence of iron is prejudicial, for the silicate of iron which would be formed in the manufacture is very dark-coloured; and it is the presence of this salt in cheap glass that gives that glass its dark colour. This colour is also sometimes given to wine glasses. In older times all window glass was greenish, because sand is seldom found quite free from iron; but the modern means of transport enable pure sand to be sent anywhere.

In a very few cases silicic acid is partially replaced by the much more expensive *boric acid.* This acid produces a very lustrous glass which is especially useful in making certain optical instruments.

As every variety of glass must contain either potash or soda, only potash glass was manufactured in older times because only potash, in the form of potashes, was available. The use of potashes was also connected with the fact that, in Germany at any rate, glass factories were generally located in forests, for not only did the forests provide fuel for heating the furnaces, but the ashes of the burnt wood provided potashes, and if more potashes were required it could easily be obtained on the spot.

After a time soda began to be used as a substitute for potash; but when the manufacture of soda was established, a cheaper substitute for potash than soda was forthcoming. We know that the first stage in making soda by Leblanc's process was the conversion of common salt into sulphate of soda. Now sulphate of soda may be used in glass making in place of soda; it is only necessary to mix the sulphate of soda with coal, or charcoal, in order that silicate of soda may be formed in the reaction with silicic acid.*

Carbonate of lime is generally used in the form of chalk because chalk is easily obtained free from obnoxious ingredients, especially free, or nearly free, from iron; some

* The reaction proceeds in this way: while the silicic acid combines with the soda the coal reacts with the sulphuric acid, which is the other constituent of sulphate of soda, and at the high temperature of the furnace the coal robs the sulphuric acid of part of its oxygen, forming monoxide of carbon, which escapes as a gas, and leaving sulphurous acid, which being also a gas passes off (see the reverse process described on p. 180). Hence none of the sulphur that was originally present in the sulphate of soda employed remains in the finished glass.

specimens of chalk are indeed perfectly pure carbonate of lime. A whole series of other bases may be used in making glass in place of lime; lead oxide is one of those that is often employed (for more details see p. 206).

Finally, the glass works melt up old glass with the materials for making new, and for this reason most of the broken glass finds its way back to the furnaces.

When the materials for making glass have been thoroughly mixed by machinery they are melted together in large pots. It is of course desired to get a high temperature in the melting ovens with the minimum consumption of fuel, and for this reason these ovens are generally worked nowadays with regenerative gas furnaces. We shall consider the arrangement of these furnaces when we are dealing with the iron industry.

The glass blower removes some of the molten glass from the furnace on the end of his rod, and by blowing into the other end of this rod he is able to cause the glass to assume almost any shape he pleases; if the object to be made is very complicated the aid of a second workman is needed. The glass blower's rod is nothing but a piece of metal tube covered with wood in the middle, so that it may be handled when hot. Since 1908, the making of ordinary bottles has been conducted by using machines invented by an American named Owen. About £50,000 was spent in perfecting the invention. The European glass makers have spent about £750,000 in acquiring the patent rights. By this method, two workmen, with three boy-helpers, can turn out 20,000 bottles daily; to do this used to require eighty glass-makers. When the glass has been shaped to the desired form it is brought, while still hot, into the annealing oven, where the process of cooling goes on very slowly over a period of a few days; if this were not done the glass would be so brittle as

to be practically useless. It should be remarked that glass for windows is made in the way described. The workman blows as large an oblong cylinder as possible; this is cut off by shears, and, being still very soft, is flattened out, and then put into the annealing oven, from which it comes as a finished pane.

The discovery, made in the seventeenth century, that glass can be cast was of great importance. For this purpose molten glass is poured on a metal table, of sufficient size, furnished with a raised edge. All those large panes of plate glass that we see in shops nowadays are made by cutting sheets of cast glass. As these sheets can be cast of considerable thickness they may be made strong enough to be used for letting into floorings to give light to rooms beneath. When used for this purpose the glass is of course not ground.

Plate glass is also used for making the glass mirrors that have completely driven out the metal mirrors of former times. Before glass mirrors were invented finely polished plates of silver, or of a very white alloy made of two parts of copper and one part of tin, were used as mirrors. But these metallic mirrors were very inconvenient because of the sensitiveness of the surfaces, especially the surface of silver, which is so easily blackened. As the reflecting surfaces of glass mirrors are protected by glass these mirrors are entirely unaffected by outside influences.

In order to make a plate glass into a mirror a sheet of *tinfoil*—that is, tin beaten very thin—over which mercury has been poured is laid on one surface of the glass. The mercury dissolves the tin, forming with it what is called an *amalgam*; and this amalgam has two properties—it reflects light admirably, and it adheres very firmly to glass. The

excess of mercury is drained away by gradually raising the plate from its original horizontal position into a sloping position; after about four weeks the mirror is ready for use.

Mirrors made in this way leave hardly anything to be desired. But the process is extremely risky to the workmen, as they are constantly exposed to the danger of mercury-poisoning by the fumes of this metal; for mercury volatilises slightly even at the temperature of an ordinary room.

Chemists have long been acquainted with another method for making mirrors besides that wherein tin amalgam is used as the reflecting surface; in this other method, silver deposited on the glass forms the reflecting surface that is required. The suggestion to use this method on the large scale came from England.

The foundation of the process—the exact chemical reactions cannot be made clear in this place—is the fact that it is possible to prepare solutions of silver from which the silver can easily be precipitated as metal by the addition of certain reagents. If the conditions are properly arranged the silver is not thrown down rapidly as a powder, but is precipitated very gradually in the form of an extremely lustrous, mirror-like coating on the sides of the vessel. In applying this process to silvering a plate of glass, the properly chosen mixture is poured on to the side to be silvered, and after a time the mirror of silver is formed. As silver is the whitest of all the metals these mirrors are superior to all others, and a mirror made by using mercury seems dark when placed beside one made by the silvering method. The description of the preparation of these mirrors shows that the manufacture is quite harmless to the workpeople. Nor is the method expensive, although silver is the metal used. Only about $2\frac{1}{2}$ grams of the metal are deposited on a square metre of surface

[about 38 grains on 10¾ square feet], and this quantity of silver costs to-day only about twopence.

The statement always holds good that potash glass is much harder to melt than soda glass. For this reason apparatus is made of potash glass especially for the use of chemists and physicists. Very great advances have been made recently in preparing the glass vessels in which so many substances are boiled in chemical laboratories; these advances are based on turning to the best account our knowledge of the chemical and physical properties of glass. The vessels must be very thin in order that they may be quickly heated equally in every part; nevertheless the frangibility of them is not great when they are handled by people who have got accustomed to working with them. Until the year 1895 it was necessary to heat glass dishes very carefully; but glass apparatus is now to be had in which liquids may be heated to about 180° to 200° C. [about 350° to 390° F.], and which may then be plunged into cold water without breaking. Such an improvement as this was hardly to be expected.

Nevertheless this improvement was cast into the shade in the year 1902. In that year it was found possible to melt pure quartz in the electric furnace to a liquid mobile enough to work with as one works with glass. Vessels made of melted quartz are not glass vessels in the ordinary meaning of the word. Outwardly they cannot be distinguished from ordinary glass vessels. Because of the difficulty of making them, these vessels are very expensive. They are quite indifferent to temperature conditions. They may be heated to redness and at once plunged into cold water without suffering the slightest hurt.

The most easily melted glass is that wherein lead oxide

replaces most of the lime of ordinary glass. This glass is extremely easily manipulated, and those prettily ornamented plates, dishes, *épergnes*, and the like that are much used are made by casting this kind of glass in moulds. Moulded glass does not of course show the sharp edges that characterise cut glass; but the price of the former is very much less than that of cut glass ware.

The name *strass* (or *paste*) is given to the glass obtained by melting a mixture of silicic acid, potashes, and lead oxide without the addition of any lime; this product is a true double silicate of potash and lead. *Strass* is extremely lustrous; indeed it sparkles so that it is used for counterfeiting various gems, by adding to it appropriate colouring material. If such artificial gems are skilfully cut and polished it is impossible to distinguish them by the eye alone from the genuine stones. But as lead glass is soft the artificial gems soon get scratched by handling, and in this respect they differ entirely from the natural precious stones.

The colouring of glass is done by adding suitable substances to the glass when it is molten; the addition of cobalt, for instance, produces a blue colour. The most beautifully coloured glass is that known as *ruby glass*, the colouring matter of which is gold added in the form of a suitable compound called *gold purple*. The quantity of gold used is extremely small. This glass is chiefly used for making delicate table ornaments and things of that character.

The artificial gems made from strass are almost without value. Naturally, chemists have tried to make genuine precious stones; they have succeeded, as we know, in making alizarin and indigo. The first successful attempt was that of Verneuil, who made rubies in 1902. Analyses have shown that rubies consist of pure alumina coloured by a trace of

chromium oxide. Pure alumina is extremely hard to melt. It acquires the special properties of the ruby when the flame of an oxyhydrogen blowpipe [that is, a blowpipe which burns hydrogen in an atmosphere of oxygen] is made to play on a pellet of alumina, placed in a small box, on to which a very small quantity of a mixture of alumina and chromium oxide falls through a sieve. A little rod is thus formed which gradually increases in breadth until the melted mass attains a weight of 50 carats [200 grains]. Until they have attained to a weight of about 5 carats, artificial rubies are not to be distinguished from natural rubies except by help of the microscope, which enables them to be differentiated by certain fine fissures. Natural rubies are more beautiful the larger they are, whereas synthetic rubies lose in fineness of appearance as they become larger; their colour seems to be glaring and coarse. An artificial ruby of 5 carats might cost about ten shillings; a natural ruby of the same weight was valued at £25, but the cost has decreased of late. In 1909, a natural cut ruby of extraordinarily fine colour, weighing 39 carats, was sold in London for £20,000.

Artificial sapphires have come into the market since 1910; these stones cannot be distinguished by any tests from the natural gems. The artificial sapphires cost about ten shillings per carat, whereas the natural stone has hitherto been worth about £10 per carat. About 15,000 carats of artificial precious stones are now made daily. One might suppose that purchasers could no longer be found. This would be so were the stones sold only as ornaments. But because of their extraordinary hardness, these artificial gems are peculiarly adapted for use in the watch-making industry, and in some branches of electrotechnics.

Finally, we must look for a moment at *milk glass*. This is

obtained by adding phosphate of lime, generally in the form of bone ash (see p. 42), to the molten glass. A clear liquid is obtained; but as the mass cools the phosphate of lime separates, and the desired opacity is thus given to the glass. Some other substances produce the same effect as phosphate of lime, such for instance as *cryolite*, which is a mineral from Greenland containing alumina and a compound of sodium and fluorine, and is quite free from iron. The milk glass made by using cryolite is especially suitable for the shades of lamps, because the flame of the lamp cannot be seen through this glass, whereas the flame appears blood-red through glass manufactured by using phosphate of lime.

We come now to *porcelain* and *pottery*.

There are certain kinds of earth found in many places which when stirred with water form a tenacious mass that can be moulded and kneaded. Such earths are called *clay*, and special names are given to different clays in accordance with their compositions and the uses to which they are put. The commonest kind of clay generally contains a good deal of sand and is coloured brownish yellow by iron. Bricks are made by working this clay into oblong pieces. When such bricks have been dried in the air they are not very durable; indeed a shower suffices to cause them to run. Still they often serve to fill in the spaces between the timbers of framed buildings.

These air-dried clay blocks are rendered durable and stone-like, they are changed into true bricks, by being burnt. The custom used to be to build up alternate layers of unburnt bricks and turf, wood, or coal into heaps, and to cover these outside with clay, so that when the combustible material was

ignited the bricks got very strongly heated. But this method led to what is called *sintering*—that is to say, the easily fusible parts of the clay became nearly liquid, and as this semi-liquid matter cooled it bound the whole heap of bricks into one mass. Inasmuch as the iron compounds in the clay are changed into the red oxide of iron during the burning the burnt bricks are red. The practice to-day is to burn bricks in what is called a ring oven, whereby a much greater effect is obtained from the materials used for heating. After a thousand years without competitors, clay bricks have found a rival in bricks made from calcareous sandstone; we shall speak of these immediately.

It is advisable to say something now regarding *mortars*, as no other opportunity will occur for dealing with the subject. The mortar that is generally used in brick buildings is a mixture of slaked lime and sand. We know that when limestone is strongly heated it separates into its constituents, caustic lime and carbonic acid (cf. p. 177). Caustic lime is a solid body which is nearly as hard as unburnt limestone; but it possesses the remarkable property of crumbling to powder when it is brought into contact with water. Burnt lime chemically considered is the oxide of the metal calcium, and this oxide has a great readiness to combine with water. A great deal of heat is produced in this process, and the oxide of calcium is changed into hydroxide of calcium, which is slaked lime. Slaked lime may be made into a kind of paste with water, and a mixture of this with sand forms ordinary mortar. The mortar hardens completely between the bricks; in doing this it combines with the carbonic acid of the air and again forms carbonate of lime. This reaction has led to the custom of burning baskets of coke in new buildings; carbonic acid is produced, and thus the setting of the mortar

is hastened. In the course of centuries the sand in the mortar, which chemically looked at is silicic acid, also takes a part in the setting process by gradually forming silicate of lime, which is an extremely hard substance. It is for this reason that old brick buildings are so very solid ; it was not the ancients who made such durable mortars—the durability results from age.

The hardness of silicate of lime has been known for long, but it was not until 1896 that a method was found for turning this to practical account. Silicate of lime is formed very slowly at ordinary temperatures, but the formation of this compound proceeds rapidly when sand is heated with slaked lime. On this fact depends the manufacture of *lime-sandstone bricks*, which dates from the year mentioned. These bricks are made by pressing into moulds a mixture of sand and slaked lime, and heating to above 100° in closed vessels. The bricks are of a fine white colour: they are so hard, and they withstand so well the action of air, water, and frost, that they can be used in building in place of bricks made by burning clay.

Ordinary mortars cannot harden except by exposure to the air, because carbonic acid is required for the hardening ; they cannot, therefore, be employed in building under water, because of the absence of carbonic acid. But if certain additions are made to the constituents of mortar—for instance, a large quantity of silicic acid and alumina—the mixture has the property of setting to a hard mass under water. Mortars of this kind are called *cements*. Such mortars were known in ancient times ; they were probably found out accidentally, as we know that limestones are often found containing large quantities of alumina, and such limestones form hydraulic mortars.

To meet the enormous demand for cements nowadays

limestone is mixed with alumina before it is burnt; and in this way any wished-for quantity of cement can be manufactured, and the supply is independent of the discovery of natural limestones containing alumina. Another method of making cement uses the slag from iron furnaces (see Lecture XI.) as raw material. The composition of slag differs from that of cement chiefly in that the former contains less lime. The slag is finely ground, mixed with limestone, and strongly heated. After grinding finely, one has cement. This process, which is another triumph of the technical use of what was a refuse substance, has been practised since 1890.

The main constituent of all clays, to which we now return, in a chemical sense, is silicate of alumina. Pure silicate of alumina is infusible in an open furnace; but its fusibility is much increased by the admixture of sand (silicic acid), lime, potash, and oxide of iron. The manufacture of glass teaches us that silicates of potash and lime, and also silicate of iron, can be melted to a glass. These constituents of clay melt when the clay is burnt, the brick sinters, and the semi-liquefied particles of glass solidify on cooling and give hardness and compactness to the bricks.

If a specimen of clay is very poor in these constituents that clay will withstand the fire; the most fire-resisting bricks are made from such clays, and these bricks are used for erecting fireproof buildings and for other similar purposes. These bricks are generally called *fire-clay bricks*.

The plasticity of clay allows of the modelling in it of the most diverse objects, so that it is not only such simple things as bricks that are made of this material.

It is easy to produce convex vessels, and vessels of other forms having circular cross sections, by working clay on

a rapidly rotating wheel. The potter's wheel has been known from very ancient times; indeed it has been in use among some peoples—the Chinese, for instance—since times earlier than those of which any written records have come down to us.

If a vessel made on the potter's wheel is baked it comes out of the oven fairly hard, but porous like a brick, and such a vessel can scarcely be used for any length of time except as a flower-pot. If a liquid is poured into a pot of baked clay the liquid soaks into and perhaps through the walls of the pot, and the vessel cannot be properly cleansed, and cannot be used for boiling food, nor for eating out of. To remedy this state of affairs, articles made of baked clay are *glazed*—that is, they are covered with a glass.

We know that lead glass is the most fusible kind of glass (see p. 206). The cheapest way of glazing pottery is therefore to mix clay with any suitable naturally occurring lead compound, to powder this mixture finely, and to cover the article to be glazed with the fine powder that deposits after the mixture has been stirred up with water. When the pottery is then placed in the oven, silicate of lead is formed by the combination of the silicic acid of the clay with lead, and being melted runs over the surface of the pots and forms a glaze thereon, so that the pots are no longer porous; after a single firing the process is finished. *Galena* is the lead compound most commonly used for glazing pottery; it is a compound of lead and sulphur, and is found native in many parts of the world. Vessels glazed in this way cannot be used for cooking, because foods which contain acids, such as those prepared with vinegar, dissolve some of the lead, and lead is poisonous. The sale of kitchen utensils glazed with lead glaze is therefore nowadays forbidden by law.

Attempts have been made in recent times so to alter the composition of these glazes as to insure that the whole of the lead is so firmly combined with other substances after firing that none of it can be dissolved by the acids contained in foods, for all cooked dishes are slightly acid in the strict chemical meaning of the term. The results of these attempts have been successful.

Stoneware is a much more durable material than ordinary pottery. The clay used for making stoneware is of such a nature that it melts superficially at a moderately high temperature, and on cooling forms a hard mass which is quite impervious to liquids. Articles prepared in this way, such as the cheap grey or brownish bottles in which natural seltzer water is sent out [in Germany], do not require to be glazed to make them impermeable by water.

But another very simple method of glazing, which gives a more agreeable and more lustrous surface, is also practised with all kinds of stoneware goods that are brought into the market. When the oven wherein the goods have been baked has been fully heated, some common salt is shaken into the fire, and the draught is shut off for a time. The oven gets filled with the vapour of salt, for common salt is not very difficult to vaporise. Now we know that common salt is a compound of sodium and chlorine ; the sodium coming into contact with the silicic acid of the clay on the surface of the vessels forms silicate of sodium, and this combined with other silicates—for clay consists essentially of silicates —forms a glass. To glaze the ordinary cheap stoneware goods, it is then sufficient to throw common salt into the oven, and the entire operation requires only a single firing.

Genuine stoneware goods, which differ from pottery in that they are twice fired, are made by selecting a very pure clay,

free from iron, and putting the goods back into the oven after they have been once fired; such goods are quite white, and the glaze they acquire is also white. Such stoneware hardly differs externally from porcelain; but the glaze, which has been produced at a lower temperature than the glaze on porcelain, soon scratches when the stoneware is used, and becomes covered with fine cracks, with the result that the vessels cannot be thoroughly cleaned and do not look well; and, indeed, stoneware dishes are not pleasant for eating off for this reason.

The temperature whereat the glaze is burnt into stoneware is not very high, and the custom is to add some borax and some oxide of lead in order to make a glaze that is sufficiently fusible. By properly choosing the mixture of lead oxide and borax the lead becomes so closely combined that acids have no solvent action upon it.

Stoneware vessels become thoroughly hard and durable by the first firing, as this is sufficient to bind the whole mass completely together. It is not necessary that the material should run again while the glaze is being burnt in by the second firing; and there is therefore no danger, as there is in the case of porcelain (see forward), of the vessels getting misshapen and losing their proper form during this process. Hence—and in this these goods differ from porcelain (see p. 219)—generally speaking only three depressions in the surface glaze are noticeable on the bottom of a piece of stoneware, which depressions mark the place where the plate or other article was supported during the burning in of the glaze. The rim on the undersurface of a porcelain plate is not glazed (see p. 219).

Fayence should be spoken of in connection with stoneware.

The name of this kind of clayware is derived from the Italian town Faenza, where the ware was first manufactured. Another name for the same kind of ware is *majolica*, from the island of Majorca, where goods of this description were manufactured in large quantities in olden times.

Fayence requires a very easily worked, plastic clay, in order that the objects—such as dishes, plates, etc.—may be properly fashioned, for it is chiefly for carrying out ornamentations in relief that this ware is used. Anything made in *fayence* is pretty sharply baked; this ware is therefore fairly hard; but as the clay is very fire-resisting, the objects run only slightly in the ovens, and their outlines remain very sharp. On the other hand, we know that a clay which has run but slightly in the fire is porous; hence if *fayence ware* is to be impermeable by water it must be glazed after it has been made. For this reason, when the ware has been once fired it is covered with some glazing material, and is again passed through the fire. Very various effects are obtained by selecting materials that produce either opaque white glazes or coloured glazes. The white opaque glazes are generally obtained by mixing oxide of tin with the constituents of the ordinary glazes.

We have now to consider the most perfect of all claywares —namely, porcelain.

Porcelain possesses many of the valuable properties of glass in a more marked degree even than glass itself. It is harder, and bears changes of temperature without cracking better than glass. On the other hand, porcelain cannot be worked into so many shapes as glass; and one has to be content with the pure whiteness of porcelain in place of the transparency of glass.

Porcelain has been known in China and Japan for a very long time. It was discovered in Europe by the Saxon adept Böttcher in 1703. At first he was able to make it only

with a brown colour; but in 1710 he succeeded in preparing pure white porcelain vessels, and these have continued to be made since that year in Meissen.

As porcelain must be pure white, and as it must be fired at the highest possible temperature in order to bring out its excellent qualities, only such clays as are quite free from iron and contain no fusible materials can be used in the manufacture. Clay suitable for making porcelain is called *kaolin*; such clay is not very common. The clay is purified by shaking it with a large quantity of water, whereby the heavier and coarser particles sink to the bottom, while the fine particles remain suspended in the water. The turbid water is poured off from the sediment into another vessel, where it is allowed to settle. The fine clay that is thus obtained will scarcely vitrify superficially in the furnace, and it is therefore necessary to add some flux to it before shaping it into vessels which are to be baked. The flux which is used for this purpose is very finely ground and washed *potash felspar*, a mineral found in nature which melts and runs to a glass at a very high temperature. The felspars are double compounds of silicate of alumina with silicate of potash or soda; they contain also some silicate of lime.

Vessels formed of a mixture of washed kaolin and felspar shrink so much when they are fired that they very often crack; but this difficulty is overcome by adding silicic acid to the other materials. Silicic acid is obtained of sufficient purity for this purpose by finely grinding and washing quartz, fireclay, or sand. The mixture of these three materials, to which some manufacturers add a fourth material that contains lime, is shaped on the wheel, like pottery, and the vessels, after being dried (whereupon they become very fragile), are heated in a furnace to a strong red heat, at which

temperature they shrink and become compact and fairly hard.

The porcelain that is prepared in this way finds only one application: it is used for the porous cells of galvanic batteries. If a liquid is placed in a pot made of this unglazed porcelain, and the pot is placed in another liquid, the two liquids pass through the walls of the pot and come into contact, and yet they do not mix, in the ordinary sense of the word *mix*; and these are some of the conditions required for producing an electric current.

Porcelain made as described must now be glazed. The glaze used for porcelain, unlike that employed for other kinds of clayware, is extremely infusible; it forms a true glass, which spreads over the surface of the finished product. The glaze consists of the porcelain material itself, with the addition of some more fusible substance, which makes the melting of the whole possible. The more fusible substance is alkali and lime, the former being supplied by increasing the quantity of felspar.

The finely powdered and washed glazing substance is stirred up with water to a thin paste, and the burnt porcelain is dipped into this, so that a sufficient quantity of the paste adheres to the surface of the porcelain. The glazing paste must be brushed off those parts of the porcelain vessel which will come into contact with the supports whereon the vessel is to rest in the oven, otherwise the vessel will be fused to the supports by the melting of the glaze. It is for this reason that we always notice a raised rim on the bottom of a porcelain plate, for instance, while the bottom of a glass dish is flat. Instead of removing the glaze from the whole bottom of the plate it is only necessary to remove it from the rim. The unglazed parts are rough, and get gradually dirty, because dirt slowly soaks into the pores and cannot be

removed by rubbing. It is possible to distinguish genuine porcelain at a glance by the presence of this unglazed rim, for such a rim is never found on the under-surface of even the best stoneware vessels (see p. 215).

In order to melt the glaze, porcelain goods are placed in the furnace a second time, and the temperature is raised to a point much higher than that at which stoneware is fired.

We know that stoneware acquires its proper hardness by a single firing, and that the hardness is not increased by the process of burning in the glaze. It is otherwise with porcelain ; the product of the first firing, known as "biscuit," is fairly hard and compact, but it is only when it has been fired a second time at a very high temperature that it becomes completely vitrified. The second firing is needed to produce that hard mass, with which the glaze is, so to say, interfused, which is able in so marked a way to resist all external influences. On the other hand, the porcelain gets so soft at this high temperature that unless each piece is supported at many places on its under-surface it is drawn quite out of shape by its own weight.

The course of the firing is regulated by taking out single trial pieces from time to time. As the glaze gradually melts it gets smoother and more lustrous ; and when it is seen by the transparency of the whole mass that the biscuit is sufficiently glazed the fire is withdrawn, and the oven and its contents are allowed to cool slowly.

Unglazed porcelain may of course be subjected to the same sharp firing as that by which the glaze is burnt in. If this is done the whole shrinks so much that it loses its porousness ; but the surface remains somewhat rough, and looks dull. Such ware is called *biscuit porcelain.* It is used for making busts, statues, and similar objects which would be spoilt by the lustre of a glazed surface.

As regards the *painting of porcelain*, two methods are adopted; the painting is done under, or upon, the glaze.

For painting under the glaze—that is, for painting the strongly heated porcelain—only those metallic oxides can be used—and there are but few of them—which will withstand the very high temperature of the second firing. One has cobalt oxide for blues, chromium oxide for greens, and oxide of uranium (one of the rare elements) for black.

The advantage of this method of painting is that the colours are indestructible; because, as they are protected by the glaze, they can be destroyed only by breaking the porcelain itself. While the choice of colours for painting under the glaze is rather limited, any wished-for shade of colour may be obtained when the painting is done on the glaze. Hence any oil painting may be copied on porcelain. This art of porcelain painting has been cultivated chiefly at Sèvres.

The proper colours, which consist, as one would suppose, chiefly of metallic oxides, are mixed with some material that readily melts to a colourless glaze—lead oxide, as we might suppose, is much used—and, after being mixed with oil, are painted on to the porcelain; and the painting is fused firmly on to the surface by heating the piece in a muffle furnace.*

The gilding and ornamenting in gold of porcelain, that were so much used in older times, were carried out in a precisely similar way. The gold, which was burnt in with a fusible substance, was dull when it came from the furnace, and required to be polished in order to make its lustre

* A muffle is a kind of box made of fireclay which is heated by a fire playing around it in such a way that the contents of the muffle do not come into contact with the smoke nor with the gases produced by the fire.

apparent. A gilding liquid was, however, discovered in 1830 —the gold being first of all dissolved in *aqua regia* (see forward, Lecture XI.)—which could be painted on to the porcelain, under proper conditions, and, after burning, produced a lustrous gold-coloured effect.

We cannot well enter upon an explanation of the phenomena that come into play in *photography*, which is the subject we now turn to, without assuming a certain amount of preliminary knowledge, because the phenomena in question rest on very complicated chemical occurrences.

In this, as in other similar cases, we shall succeed best by making the historical development of the subject the basis of our treatment. By doing this we see the gradual perfecting of the subject, and we have the opportunity of passing rapidly in our own minds through the most important stages of thought which have brought the art to the high position it occupies at present.

Silver dissolves easily in nitric acid to form a colourless liquid. When this solution is evaporated a white salt is obtained. This salt is called *nitrate of silver*; it is also often known as *lunar caustic*.

Anything that is rubbed with this salt soon becomes black when exposed to daylight. The human skin, for instance, is blackened by it, and lunar caustic is often used in this way as a cautery. If a solution of the salt is thickened with gum, and letters are written with this liquid, the letters come out black after a little time. Such writing can scarcely be removed, certainly not by washing; a solution of lunar caustic therefore serves as an indelible ink. The reason of this appearance is that nitrate of silver is very ready to decompose

into its two constituents—the decomposition is, indeed, effected by exposing the salt to daylight—and in this decomposition the metal silver separates as an extremely finely divided black powder.

This property of the salt has been known for a long time; but it cannot be made use of for obtaining pictures, because the decomposition is much too slow for that purpose.

The preparation of pictures was first accomplished by using certain salts of silver which are much more quickly changed by light than the nitrate is. And the three salts that have been most used in photography are the *chloride*, the *bromide*, and the *iodide of silver*. These three are all easily prepared. As these salts are quite insoluble in water, they are thrown down when chloride of sodium (common salt), bromide of potassium, and iodide of potassium, respectively, are added to a solution of lunar caustic. In the case of common salt, for instance, chloride of silver and nitrate of sodium are produced; thus

Nitrate of silver + chloride of sodium = chloride of silver + nitrate of sodium.

Nitrate of sodium is known to us as a salt that is very easily soluble in water (see p. 50); hence it remains dissolved in the water in the foregoing reaction, and therefore the chloride of silver can be completely freed from nitrate of sodium by washing with water.

Chloride of silver has been known for long; bromide and iodide of silver have been known since the first quarter of the nineteenth century, at which time bromine and iodine were discovered (see pp. 46 and 51).

The alchemists made great use of chloride of silver. It is very sensitive to light, for immediately it is exposed thereto its pure white colour begins to change to violet, and this

darkens until finally the colour becomes black. A physician of Halle named Schultze was the first to employ this salt, in 1727, for producing pictures. He laid letters cut out of paper on a freshly made precipitate of chloride of silver spread on a flat surface. Only the exposed parts became darkened, and on removing the paper the letters appeared white on a dark background; but in a short time the letters also became black, owing to the action of the light. All one can say of this experiment is that it furnished an interesting observation, but that it was not of any practical utility.

It was not until a hundred and twelve years after this that Talbot, in 1839, obtained actual pictures by using chloride of silver. His procedure was as follows. He dipped paper into a solution of common salt, and then brushed a solution of nitrate of silver over this paper. The paper now contained chloride of silver. On the paper prepared in this way he laid a transparent drawing, and exposed the whole to sunlight. The chloride of silver darkened the most in those parts where the greatest amount of light was able to penetrate through the transparent drawing. Had Talbot now removed the drawing the light would of course have darkened the whole of the paper—that is, Talbot would not have advanced on what had been done by Schultze. But the great improvement made by Talbot was that he found out a method for binding, or fixing, the picture which had been formed. He took the sensitive paper, whereon the sun had produced an image of the drawing, into a darkened room, and there placed it in a boiling solution of common salt. Now chloride of silver dissolves in a boiling solution of salt. The unchanged chloride of silver left on the paper was thus removed, and the drawing remained imprinted on the paper, inasmuch as chloride of silver which has been blackened by sunlight is

so chemically changed that it is not dissolved by a solution of common salt.

A consideration of what has been said will show that the picture obtained in the way described must be a negative copy of the original drawing, for the dark parts of the drawing let less light through them than the lighter parts. The chloride of silver that was covered by the darkest parts of the drawing remained quite unchanged, and was therefore removed by the treatment with salt solution, so that these parts appeared white, or nearly white, while the parts covered by the lighter portions of the drawing appeared dark. But Talbot now laid this negative on paper made sensitive by chloride of silver, and, by repeating his treatment, obtained an accurate copy of the original drawing.

Talbot's process was evidently only a photographic method of multiplying the original drawing; but Daguerre, also towards the end of the thirties of last century, brought to completion a method for obtaining pictures by means of photography. Daguerre is, therefore, the true discoverer of what we now call photography. He used the *camera obscura* to obtain direct delineations of objects, without starting from pictures of these objects. The *camera obscura* is an apparatus by which pictures of objects placed in front of the instrument are produced, by the use of lenses, at a definite spot where a plate of roughened glass has been placed for the purpose of focussing the picture. In place of the plate of roughened glass, by the help of which the apparatus was sharply focussed on the object to be photographed, Daguerre put a plate of silver on which some iodide of silver had been formed by the action of vapour of iodine. The photographic plate in the camera, in conjunction with the lens, may be regarded as an artificial substitute for the

retina of the eye. What may be called an artificial eye was thus formed, which could be extended in many more ways than human eyesight. A picture appeared on this plate after the action of light had been allowed to continue for about an hour; but Daguerre had the greatest difficulty in fixing the picture, and it was an accident which first helped him to get over this difficulty. He noticed that when a plate which had been exposed to light for a short time only was brought into the vapour of mercury most of the mercury was deposited on those parts of the plate which had been most illuminated, and the picture stood out, so to say, in lustrous mercury. The mercury vapour *developed*, on the silver plate, the picture yet invisible to the human eye. Hence comes what seems to us nowadays the very remarkable appearance of those old *daguerreotypes*, as pictures of this kind were called, which are still to be found in many families.

This discovery made it possible to get photographic representations of living sitters. To obtain the likeness of a person all that was now necessary was that the sitter should remain still for a short time; and to-day people can be photographed when in rapid motion.

The part of Daguerre's discovery that must always be of most importance is the following. Although the human eye is unable to perceive any change in a sensitive plate that has been exposed for a very short time in the *camera obscura*, nevertheless the chemical action of the rays of light has brought about a decomposition of the silver compounds on the plate, and in order to develope a negative picture from such a plate it is not necessary to continue the exposure until the decomposition is completed, but it is sufficient to treat the plate with a suitable reagent, such as vapour of mercury, which is the only reagent of this kind we have as yet become acquainted with.

An enormous sensation was caused by the production of pictures by a process that was kept secret. After a brilliant lecture by the physicist Arago, the French Chamber of Deputies, in 1839, voted a pension to Daguerre and his coadjutor Niépce, on condition that their process should be made public.

Attempts began to be made at once to find a substitute for the expensive silver plates of the daguerreotype process, and Talbot was successful in using his sensitised paper in the *camera obscura*. He sensitised his paper with iodide of silver in place of chloride of silver by drawing it through a solution of iodide of potassium after it had been soaked in a silver solution.

Talbot now made use of a solution of *hyposulphite of soda*, in place of a boiling solution of sodium chloride, for dissolving the unchanged iodide of silver that remained on the paper after exposure; this salt dissolves chloride of silver, as well as bromide and iodide of silver, very easily in the cold, and it is now always employed for the purpose for which Talbot used it. But the roughness of even the best paper made itself unpleasantly apparent in Talbot's process, and it seemed as if the pictures produced by Daguerre's method on polished silver plates would gain the victory. Matters were, however, altered by Niépce's introduction into photography of solutions of albumen. If iodide of potassium is added to a solution of albumen, and this liquid is poured on to glass plates, which are then dried, and afterwards dipped into a solution of nitrate of silver, a perfectly smooth film of albumen is formed on the glass, and this film is sensitive to light because of the iodide of silver which it contains; moreover, this film has none of the roughness of paper, and it is capable of yielding excellent pictures.

The pictures produced in the *camera obscura* are negatives, and they must therefore be transferred to sensitised paper, as was originally done by Talbot, to produce positives—that is, true representations of the objects photographed. From this time onwards the paper to which the negative was to be transferred was covered with a sensitised film of albumen, and very finished results were obtained because of the smoothness of the surface and the consequent brilliancy of the picture produced thereon. But solutions of albumen have an unpleasant readiness to putrefy; this led to the substitution of collodion for albumen, as recommended by Fry. *Collodion* * is a solution of nitrated cotton wool, that is guncotton (see p. 125), in a mixture of ether and alcohol.

The invisible change that is brought about by a brief exposure to light, which Daguerre had succeeded in fixing by means of vapour of mercury, must and can be fixed, as we have already mentioned, on those plates which are used in place of the silver plates of Daguerre. The substances that are employed for doing this are classed together under the name of *developers*. The developers that were used in the earlier days of photography were *ferrous sulphate* (commonly known as *green vitriol*) and *pyrogallic acid*. All sorts of chemical substances have been tried from time to time; of these *hydroquinone* has been found to answer especially well.

In the collodion process, which we shall now consider, a glass plate is covered with collodion mixed with bromide and iodide of potassium, and is dipped into a solution of nitrate of silver; the wet plate, which contains both bromide and iodide of silver along with some adhering nitrate of silver, is then exposed in the camera. If the plate is brought,

* This substance was first employed, by Maynard, as a glue; hence the name collodion, from κόλλη = glue.

after exposure, into a solution of green vitriol or pyrogallic acid (in the dark room), this reagent reduces the excess of silver nitrate to silver, but it does not act on the bromide or iodide of silver on the plate. The silver which is thus separated from the nitrate of silver as a fine powder deposits itself on those parts of the plate which have been exposed to light, in proportion to the amount of light that reached the different parts, just as the vapour of mercury did in the daguerreotyping process. The result of this procedure is that the negative becomes visible. The fixation of the negative, and the removal of the excess of bromide and iodide of silver, is brought about by immersing the plate in a solution of hyposulphite of soda, which dissolves and so removes the bromide and iodide of silver. The process may be called an acid process in the chemical sense inasmuch as pyrogallic acid is employed. Attempts were made to prepare in this way dry plates which might be stored and used at any time, but without success.

In 1860 Russell found that the effect of light on the precipitate of silver bromide and iodide on the plate contained in the *camera obscura* could be made visible without the presence on the plate of any excess of silver nitrate. If the excess of silver nitrate is thoroughly washed away from the wet plate by a large quantity of water, and the plate, after exposure, is immersed in an alkaline solution of pyrogallic acid (that is, in a solution prepared by adding alkali to the pyrogallic solution used in the older process), the alkaline pyrogallate acts upon the bromide and iodide of silver—this, we know, the solution without addition of alkali did not do—in proportion to the amount of light that has fallen upon the plate, and a picture is produced, which can be fixed by hyposulphite of soda, which removes

the unchanged bromide and iodide of silver. This discovery brought nearer the possibility of making dry plates, inasmuch as it was no longer necessary to leave an excess of a solution of silver nitrate on the plates.

It was soon found that alkaline pyrogallate solution acts much better on bromide than on iodide of silver; and it is for this reason that bromide of silver has become so important in photography.

Maddox in 1871 recommended the employment of gelatin in place of collodion; but the true discoverer of the gelatin emulsion process, which has now gained complete supremacy, was Bennett, in the year 1878. Bennett showed that a silver bromide gelatin emulsion gains that high degree of sensitiveness for which we praise such emulsions to-day only after prolonged warming. The preparation of the dry plates that are used to-day is based on the employment of gelatin and on the observation made by Bennett; the process is as follows.

Bromide of ammonium (in place of the bromide of potassium formerly used) is dissolved in water, in a dark room, and gelatin and then nitrate of silver are added, the temperature being at first kept at 75° C. [167° F.], but afterwards raised to boiling; bromide of silver is thus formed. Everything that will dissolve in water is washed out of the silver bromide gelatin emulsion thus produced; the emulsion goes solid on cooling; after washing, it is liquefied by heating, and poured on to glass plates, which are dried as quickly as possible in drying racks, and are then ready to be sent into the market. They are packed in a dark room, in such a way that it is impossible for light to get at them until they are used in the camera. The plates prepared in this way are about ten times more sensitive than the old-fashioned wet collodion plates.

The great development of amateur photography began with the manufacture of these plates. The preparation of sensitised plates, which up to that time had been the most difficult operation in photography, was taken away from the photographer and relegated to the manufacturer.

Excellent pictures are readily obtained by the use of dry plates provided the camera is furnished with good, and therefore expensive, lenses; and the exposure need not exceed a second, so great is the sensitiveness of these plates. The decomposition of the bromide of silver which is started at those parts of the plate whereon the light has fallen, and which is too slight to be detected by the human eye, is carried to the desired extent by the developer. As soon as it is seen, by examining the plate in the red light (see forward) of the dark room, that the development has proceeded far enough, the bromide of silver which has been unacted on is removed by immersing the plate in a solution of hyposulphite of soda, and the negative is finished. The negative is then transferred to sensitised paper, and we obtain that representation of the original object which is known as a photograph.

The greatest inconvenience for amateur photographers is the need of a dark room. Recent attempts to abolish this need have been fairly successful, and it looks as if it will be possible to produce photographic pictures without using a dark room.

The whole art of photography evidently rests on the chemical action of light on easily decomposable salts, the most important of which are to-day the salts of silver. Now the science of physics tells us that white light consists of the different colours which become visible in the rainbow,

If white light is broken up by means of a prism into its coloured constituents, and if attempts are made to photograph the spectrum thus obtained in the ordinary manner, it is found that scarcely any effect is produced on the photographic plate by the red rays, but that the greatest effect is produced by the rays at the other end of the spectrum, that is, by the violet and the ultra-violet rays. The ultra-violet is that part of the spectrum which comes after the violet part; it is not visible to the human eye, to which it appears black, but it acts on the photographic plate. This behaviour of the colours of the spectrum towards sensitive plates explains why the development of the plate taken out of the camera can be conducted in red light without the plate being affected.

In the same way it is found that yellow and green light, as well as red light, act only very slightly on the plates. This fact, which is very troublesome in attempts to reproduce oil paintings photographically, makes itself apparent in portrait photography so far as the clothing of the sitters is concerned. For this reason it is necessary to correct the photographic pictures of coloured objects, especially of portraits; the correcting process is called *retouching*.

Vogel found that this inconvenience could be avoided by adding very small quantities of certain dyes to the silver bromide gelatin plates themselves. The plates are thus made sensitive to colours which do not affect plates that have not been subjected to this treatment, as the silver bromide on the specially prepared plates is acted on by light of the same colour as that of the dyes which have been added. It is only since that discovery that it has become possible to produce those beautiful photographic presentments, especially of oil paintings, that we are accustomed to see to-day. The older photographs, or those produced with the ordinary dry plates,

show large portions of the originals only in a vague and indefinite manner. We may therefore look on the main part of the problem of reproducing coloured objects photographically in black in a proper manner as solved by the use of *orthochromatic plates*.

But another thing remains to be done, and this is quite different from the problem we have been considering, although the two are often confused, and that is to produce photographs in colours. We shall consider the solution of this problem, which was accomplished in 1907, after dealing with pigment printing.

Coloured objects can now be most successfully reproduced in colours by a process known as *pigment printing*; but this process, as its name signifies, is not a purely photographic method.

The following is the foundation of the process. It has already been stated that, besides the sensitive salts that have been enumerated, there are many mixtures which are sensitive to light. For instance, if a solution of *bichromate of potash* is mixed with a solution of gelatin, and the sun is then allowed to shine upon any object which has been washed over with this liquid, it is found that the gelatin, which was before soluble, very quickly becomes insoluble in water. The cause of this is that the light acts upon the bichromate of potash in such a way as to change some of it into an oxide of chromium, which acts on the gelatin like a tanning agent and produces insoluble substances. We have already learnt something of the attempts that have been made to prepare chrome leather directly (see p. 142). If then a photographic negative, obtained in the ordinary way, is laid in the dark on paper covered with chrome-gelatin, the parts which the light reaches will become insoluble; and if the unattacked portions of the chrome-gelatin are now removed

by washing with water in the dark room, a picture is obtained which is not black, like those formed when silver paper is used, but is nearly invisible, because it is merely of the colour of the gelatin. But there is no reason why the gelatin should not be coloured with a suitable pigment before the process is carried out. Yellow gelatin will yield a yellow picture, red gelatin a red picture, and blue gelatin a blue picture; and if the three transparent delineations that are thus obtained are fastened over one another—and they must fit exactly each on the other as they are all obtained from the same negative on a sensitive plate—the most remarkable results are produced.

The theory of mixed colours, as developed by physicists, predicts that very brilliant results should be obtained by this method as regards the true rendering of the colours of the original objects, and the performances have nearly realised these predictions. Although the process may appear from the description we have given of it to be very simple, yet the difficulties which have to be overcome in practising it successfully are very great. The process is often conducted by taking three negatives, a red, a blue, and a yellow glass plate being placed, successively, before the lens of the camera. The three negatives are then changed into positives; and these are coloured with the same dyes as were used for making the plates sensitive (see p. 231), and are then printed on one another.

There are many other reproduction methods, some of them actually in use, others in the stage of being tried; but we cannot go into these methods now. They all demand the formation of a negative by means of the camera—that is, they all begin with a representation of an object by photographic methods, and inasmuch as they do this they are all legitimate children of photography.

Many investigators of the first rank have attempted to solve the problem of producing photographs of coloured objects in the true colours of these objects. The brothers Lumière were the first to accomplish this aim, in a way which is always applicable, in the year 1907. Their process enables portraits to be taken in a studio in 20 seconds, with a clouded sky; and the picture can be developed in 2½ minutes in the dark room. They prepare their plates so that two parts of green-coloured starch granules are intimately mixed with one part of red- and blue-coloured granules. The colour of the mixture is pure white. The mixture is distributed over the surface of a glass plate, which has been coated with a sticky substance, in such a way that no starch granule is superimposed on another. The granules are carefully smoothed by a press, so as to form a continuous layer. This light-filtering layer is varnished, and a sensitive emulsion of silver bromide is spread over the varnish. When the plate is dry it is placed in the camera in such a position that the light which comes through the lens must penetrate the glass plate and the light filter of starch granules before it reaches the emulsion of silver bromide. When the plate is subsequently developed, a coloured photograph is obtained which leaves little to be desired so far as correct colouring is concerned. The procedure is so simple that amateur photographers can work it without trouble. German colour-films (not glass plates) have come into the market since 1910. These form a valuable addition to the materials for making coloured photographs.

We cannot bring to a close our consideration of the photographic reproduction of objects without drawing especial attention to the most striking advance in this department—that, namely, connected with the *Röntgen rays*—although that

advance belongs rather to physics than to chemistry. Even in the first lecture we had to make an excursion into the domain of physics in order to gain clear notions about the atmosphere.

We all know that electric sparks, whether as lightning or artificially produced, pass from one place to another not by a straight but by a zigzag course. It is the resistance that the air opposes to the passage of the sparks which produces this effect. But if the sparks are allowed to pass inside a glass tube from which the air has been so completely pumped out that the internal pressure does not amount to more than about one thousandth of an atmosphere—wires having been fused through the glass at the two ends of the tube to serve as the poles of an electrical arrangement—then the tube is illuminated throughout the whole of its length when the sparks pass, inasmuch as the resistance of the air scarcely comes into play. Wonderfully beautiful colour effects are obtained by using tubes of the kind described containing very minute quantities of different gases, such as hydrogen and oxygen, which radiate light of different colours. These tubes are called *Geissler tubes*, from the name of the celebrated glass-blower Geissler, who was the first to make them in perfect condition. If the attenuation of the air in such tubes is carried so far that the pressure does not exceed one-millionth of an atmosphere, which is much less than the pressure in the Geissler tubes, other phenomena are noticed when electricity passes. The whole tube is not illuminated, but bundles of rays proceed from that one of the poles which is called the *kathode*, while colour phenomena are scarcely noticeable at the other pole, which is known as the *anode*. If a vessel of the form shown in fig. 18 is substituted for a tube, the *kathode rays* do not altogether pass to the anode, but they proceed in straight lines, without being influenced by the anode, and produce a bright spot

where they impinge on the walls of the vessel, and, at the same time, the kathode rays partly change into Röntgen rays.

In the year 1895 Röntgen made an investigation of the kathode rays outside of the tube* wherein they were produced, carrying out his research in a darkened room. Having completely encased the bent tube in black pasteboard, he placed a paper, over which was spread a solution of *platinocyanide of barium*, in such a position that if the kathode rays were produced they would strike upon this paper, and he noticed that the paper began to *fluoresce*, with a yellow colour, and therefore to become visible in the darkened room. Here then he had to deal with a new and most interesting kind of rays, very different from those ordinarily visible to the human eye, and capable of passing through a covering of black pasteboard. The existence was revealed of rays which the human eye cannot see directly, but only in the form of fluorescence-phenomena produced by them, and which act through a black covering that stops the kathode rays.

By fluorescence is signified the property which many substances possess, among these being platinocyanide of barium, of converting the ultra-violet rays (which we have already mentioned) into visible rays of light; the greenish sheen that is noticed in most kinds of petroleum, for instance, is due to fluorescence. The Röntgen rays resemble the ultra-violet rays contained in ordinary light in that they occasion fluorescence. The fluorescence of the paper we have spoken of must have been the effect of some cause having its origin in the tube, which was completely covered, wherein the

* Röntgen at first used tubes of the form shown in fig. 18. Although many modifications have been made in the form of the tubes, the oldest form is retained here, inasmuch as the principle has not been altered.

kathode rays were produced. It must be due to some kind of rays which are produced along with the kathode rays, but differ from these rays; which are not perceived by our eyes; which differ from all rays previously known, in their power of passing through black pasteboard. It was also found that a book or a wooden board placed in the produced direction of the kathode rays did not stop the fluorescence of the barium platinocyanide paper when that was held on the other side of the obstruction; hence the rays are capable of passing directly through such things as a book or a piece of wood.

Röntgen placed a sensitised photographic dry plate in the

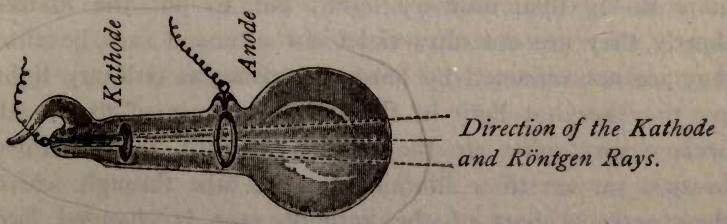


Fig. 18.

place where the paper had been, and he found that this plate was acted on, in a completely darkened room, by the rays that are invisible to the eye; moreover, when he brought various substances more solid than paper or wood between the plate and the tube wherein the rays were produced, shadow pictures of these substances were obtained on the plate when that had been developed in the usual way.

Inasmuch as the rays pass through relatively soft flesh but not through much more compact bones, a shadow picture of the bony skeleton of the hand is obtained by exposing the hand to the action of these rays.

Photographs can be taken with the Röntgen rays in ordinary daylight, for it is only necessary to place the

sensitised plate in a black box, and to lay the object—the hand, for instance—on the top of this box while the rays are allowed to fall on to the object; the rays pass through the wood, which, however, protects the plate from daylight, on to the plate inside. These rays are not refracted by lenses; hence pictures obtained by their use are true and accurate shadow pictures of the same size as the original objects, in distinction to photographs proper, which permit of the representation of a large landscape on a space not more than one or two inches square because ordinary light is refracted in passing through lenses.

The Röntgen rays act on sensitive silver salts, but much more slowly than ordinary light; but, to put the matter shortly, they are not ultra-violet nor ultra-red rays, because they are not refracted by lenses or prisms, as ordinary light is; they are not light in the ordinary sense of the word, because we cannot see them; they are not kathode rays, because we see these illuminating the tube through which they pass; a part of the kathode rays is changed into Röntgen rays by impinging on the glass wall of the vessel. They are something altogether new; and what is to be the value of this new thing, whether for science or for ordinary life, we must learn fully at a later time.

These rays have already proved so useful in surgery that the means of producing them has become a necessary part of the surgeon's apparatus for detecting fractures in bones, the presence of foreign substances, etc. The rays are also used as a curative agent in some cutaneous diseases.

In 1896 Becquerel set himself to discover whether an inversion of the phenomena of the Röntgen rays was possible; that is, considering that these rays produce fluorescence, whether fluorescent substances could produce Röntgen rays. He placed different fluorescent substances on photographic

plates which were shielded from the action of ordinary light. On developing the plates, he found that many compounds of the element uranium had impressed their photographic images on the plates, through the black paper. The compounds of uranium had emitted rays unrecognised until then. These rays showed themselves to be different from Röntgen rays, for instance, in that on taking a photograph of the hand, an outline appeared of the whole hand, but the bones were not visible. Thereupon the search began for substances which acted like uranium compounds, for *radio-active* substances. The mineral *pitchblende* found in Joachim's Valley in Bohemia was found to possess this property. This mineral contains many chemical elements ; investigation showed that the radio-activity of pitchblende was connected with the presence in it of barium. It has been found possible to decompose the radio-active constituent and to obtain a substance more radio-active than any previously known ; this substance was named *radium* by its discoverer, Curie. One gram [30 grains] of radium chloride—which is the compound that comes on to the market—costs about £16,000 ; it is sold by the milligram. Hence one can have a notion of the labour needed to extract from pitchblende the minute quantities of radium that are found in that mineral.

The more minute investigation of radium soon revealed such remarkable properties, so different from those which belong to any substance known to science, that the behaviour of radium seemed for a time to be inexplicable. All the ordinary methods of investigation and the ordinary theories seemed to be inapplicable. The most astonishing thing about radium is that it is constantly undergoing change, and sending out rays of a very extraordinary character. The name *emanation* has been given to these rays. Inasmuch as the emanation of radium has been obtained in the form

of a liquid, it is evident that the emanation is not really a collection of rays, but has something material about it. One may speak of it as a stream, as one speaks of a stream of water. Radium emanation is found in all those springs of water which long experience has shown to possess healing properties, which properties cannot be connected with any other of their chemical constituents. The secret of the springs at Gastein, Baden-Baden, Kreuznach, and elsewhere [including those at Bath] is thus elucidated; and a reason is found for the fact that these waters are efficacious only when used at their sources. For the emanation is very mutable, and disappears from the waters after a short time. An apparatus is now to be found in druggists' shops, the radium-containing material of which gives off emanation to water stored therein, so that water charged with the emanation can be drunk in these shops. The aggregate rays given off by radium exert a very marked and directly destructive action on the skin; nevertheless, they are useful as a curative agent in certain skin diseases.

LECTURE XI

Noble and base metals—Ores—Gold—Platinum—Potassium cyanide—Silver—Relations of value between gold and silver—Bimetallism—Gold currency—Reduction of metallic oxides—Roasting sulphur compounds—Pig iron—Steel—Wrought iron—Blast furnaces—Slags—Coke—Puddling—Rolled iron—Railways—Cementation steel—Cast steel—Bessemer steel—*Spiegeleisen*—Manganese—Dephosphorising iron—Soft steel—Nickel steel—Chromium steel—Gas furnaces—Regenerative furnaces—Open flame furnaces—Zinc—Electro-deposition of metals—Potassium—Sodium—Aluminium.

WE are accustomed to speak of two great classes of metals, the noble and the base metals. The chief difference between these classes is that the noble metals are very slightly acted on by other elements, especially by oxygen and sulphur, which are most frequently taken into consideration because of their abundant distribution on the earth's surface, whereas the base metals soon succumb to the attack of other elements, or, to express it otherwise, very readily enter into chemical combination with other elements. The noble metals, as we should expect, generally occur uncombined in the earth, and they are therefore relatively easily obtained from their deposits; whereas the other metals have been converted in the course of endless ages into oxides by the action of oxygen, or into sulphides by the action of sulphur, or they occur in the form of yet more complicated combinations.*

* Miners call the sulphur compounds of metals sometimes *pyrites*, sometimes *glances*, and sometimes *blendes*. The first two have a metallic habit—lead glance, for instance; the last—zincblende, for instance—has not.

That the base metals may become serviceable to mankind they must be separated by some means or other from the substances that mask them. The naturally occurring compounds of such elements are spoken of as the *ores* of the metals, when these are found in any spot in quantities sufficient to make the technical extraction of the metals therefrom profitable.

It is only in poetry that the word *ore* is used as synonymous with metal; in practical affairs it is always taken to mean, not the metal itself, but any compound of a metal which is found in nature.

It would be of little use for us to speak of all the metals in this place. In addition to certain points connected with the noble metals, we shall deal in detail only with the preparation of iron, which is the most important metal in ordinary life. And in doing this we shall be able to gain some insight into the extraction of metals generally.

Gold and *platinum*, which are noble metals in the chemical sense, occur almost solely uncombined in the earth. Gold and platinum also are found in the sands of rivers, or in other deposits of sand, and they are obtained by washing these sands. When gold is found imbedded in hard rocks these are stamped and ground, and the metal is extracted either directly by washing with water, or by the help of mercury or potassium cyanide, which dissolve gold.

In South Africa, for instance, the gold-bearing rock—which contains about 40 to 50 grams of gold (worth £2 to £2 10*s.*) in 1,000 kilograms, equal to about only 0·002 per cent. of gold—was at first stamped, with addition of water and mercury. The mercury dissolved the gold; the amalgam was distilled, whereby the mercury was removed, and the gold remained in the retorts. A considerable quantity of

gold, however, remained in the crushed rock. In the nineties of last century Forest introduced the method of lixiviating the residue with a solution of potassium cyanide, which removed almost the whole of the gold. The residual crushed rock is placed in vats, made of cement, holding about 400,000 litres [about 90,000 gallons] and covered with a dilute solution of potassium cyanide; air is driven through the liquid (the oxidising action of air is needed for the reaction), and the gold is dissolved. Zinc which contains lead is placed in the solution drawn off from the residual solid matter, and as this goes into solution the gold is precipitated. This process proved itself to be so successful that it is now used in many places for the treatment of gold-bearing rocks which are so poor in gold that the extraction of gold from them could not be made remunerative by any other process. Without doubt the cyanide process is the greatest advance that has yet been made in the gold industry; it has done much to bring about the great increase which there has been in the output of gold.

The extraction of silver, except in those places where it occurs native, is by no means so simple that it can be clearly set forth here; we shall not therefore go into the methods, which are moreover all special methods for this metal, notwithstanding that the chemical improvements made in these processes have very largely contributed to the sudden fall in the price of this metal. It will be of more interest for us at present to pay some attention to the question of the relative values of the two metals, gold and silver.

The oldest tidings that we have on this matter come to us from about seven hundred and ten years before Christ. A plate of gold and a plate of silver have been found in the

foundations of the palace of King Sargon, who flourished about that time in the Assyrian city of Khorsabad, and these plates bear inscriptions that 1 lb. of gold was worth $13\frac{1}{3}$ lbs. of silver in those days. It is very remarkable that this relation of values is found to be approximately maintained at all later times—for instance, in ancient Rome and also during the Middle Ages. The exact relation between the values of the two metals is known from 1687 onwards, because the merchants of the London and Hamburg exchanges have continued to record this relation since that year.

We find that the relation between the two metals fluctuated only very slightly until the year 1874; putting the figures into weights, 1 lb. of gold was able to purchase, on the whole, as much as $15\frac{1}{2}$ lbs. of silver. But matters changed in 1874. The enormous output of silver from America, which seemed for a time as if it would be exceeded, if that be possible, by the supply coming from Australia, threw such quantities of the white metal on the market that the supply far exceeded the demand.

It does not much matter whether in such a state of affairs one has to deal with a white metal or a red metal—the price of copper, for instance, has been affected like that of silver by over-production—or with grain, whatever is thrust on to the market must be allowed to go at a lower price; and so we find that the enormous increase in the production of silver, without a corresponding increase in the demand, has caused the price of this metal to fall gradually. When silver was cheapest, it was possible to get 37 lbs. of silver for 1 lb. of gold.

The relations between gold and silver are affected in the way we have described when these metals are regarded as commodities, for these relations are influenced by the same

causes as those which at any time and place influence the relative values of commodities in general.

The total amount of gold produced between the years 1492, that is, from the discovery of America, and 1900 was 37,231,900 lbs. Troy; and the total amount of silver produced in that period was 697,048,168 lbs. Troy (260,092,600 kilos.). The more exact numbers for the last 40 years are as follows:

Years.	Gold.	Silver.
1871–75 ...	463,908 lbs. Troy.	... 5,253,550 lbs. Troy.
1881–85 ...	397,819 „	... 7,633,765 „
1891–95 ...	654,027 „	... 12,074,755 „
1901–5 ...	1,367,496 „	... 14,124,296 „
Year.		
1906 ...	1,620,957 „	... 13,786,147 „
1907 ...	1,655,564 „	... 15,503,181 „
1908 ...	1,729,028 „	... not yet known accurately
1909 ...	1,806,837 „	...
1910 ...	1,825,080 „	...

1 kilo. (2·68 lbs. Troy) of gold is worth £139 10*s.*, and 1 kilo. of silver about £3 12*s.* at present.

But the relations between gold and silver become much more complicated when one considers the money that is coined from the two metals. We shall refer to the compositions of coins in Lecture XII. when we are dealing with alloys.

The Greeks and Romans had on the whole as much gold as they needed for their coinage. There are no direct complaints of the shortage of gold to be found in their writings. But the wanderings of peoples which destroyed the culture of the ancient world, from about the year 375 A.D., and brought the mining industry everywhere to grief, so affected the supply of gold that a great scarcity of this metal made itself felt. This scarcity of gold was the cause of the rise of alchemy; this it was that spurred on human activity to the endeavour to make gold artificially,

in order to obtain the most convenient mediums of exchange for all commodities, and the most convenient basis for commercial transactions. The aim of the alchemists was not attained; gold cannot be made artificially. The vast amount of work which was expended in the quest led to the accumulation of much chemical knowledge, from which chemistry at last emerged as a science. In the great empire established by Charles the Great, about 800, political relations were again made so stable that a general demand arose for a coinage which should be current everywhere. As gold could not be obtained in sufficient quantity, the only available metal was silver. Charles the Great issued an edict concerning coinage, based on silver as a standard. The pound (*libera*) of silver was divided into 20 parts, each of which was called a *solidus* (shilling). Each solidus was subdivided into 12 parts, called *denar* (pence). This is the coinage system used in England to-day. The difference is that one pound sterling is now worth [20 shillings] about 20 marks, while a pound of silver was worth about [80 shillings] 160 marks from the time of Charles the Great until about 40 years ago. The reason for this downward movement in the value of a pound sterling is simply the fact that the English kings debased the value of their coinage, in the Middle Ages, when there was a great demand for money.

The French kings carried the debasing of coinage further than the English. At the beginning of the Revolution they had reduced the *livre* (*libera*) to the value of 4 marks. The Italian *lira* is worth to-day only about 80 pfennings [8 pence].

Gold money was first again coined in Europe in Pisa, Genoa, Venice, and other city-states of Northern Italy. The extensive trade between these states and Asia Minor, especially the Levant, gradually brought them so much gold

that their mints became a remunerative business. Florence made a beginning in 1252. Hence the designation of gold coins as *Floreni*, or *Fiorini*. The name *Ducat* came in somewhat later; the word comes from the Italian title *Duca* (duke). Gold coins were also called *Zechins* [or *Sequins*] from *Zecca*, Italian for the mint.

As long as the ratio between gold and silver remained as good as constant—and so far as those who are now living are concerned this was until about the year 1874—it did not seem to matter whether a man possessed 1 lb. weight of gold money or 15½ lbs. weight of silver money—calculated on the quantity of pure gold or silver in either—for he could exchange the gold money for an equivalent quantity of silver money, or *vice versâ*, at any time he pleased.

That was the era of legitimate bimetallism. As both metals served equally well (for coinage) on account of their relatively high intrinsic values, the different states coined the two metals in the ratio by weight of 1 to 15·5. Nevertheless, bimetallism got into difficulties. The continuous, although small, fluctuations in the relative values of the two metals made it difficult to deal with the necessary commercial payments in the more advanced communities. The history of bimetallism in England since the middle of the sixteenth century shows this clearly. In 1816 England adopted a gold standard. But when the time came that 16 or 17 lbs., or even more, of silver could be obtained for a single pound of gold, it was of course necessary that the states should soon close their mints against the coinage of silver brought to them by private individuals. For if the states continued legally bound to coin the same amount of money from 15½ lbs. of silver as from 1 lb. of gold, it would be possible to buy 15½ lbs. of uncoined silver for, let us say, nine-tenths of a pound of gold, and indeed for a weight of gold which constantly kept getting less; if there-

fore they had gone on as before, all the gold coins would gradually have been driven out of the countries in question. For the dealers would have sent these gold coins to other countries where they could buy for 1 lb. weight of them—always calculated on the pure metal in the coins—not $15\frac{1}{2}$, but perhaps 30, or even more than 30 lbs. of silver, which silver they would have brought back to the states in question for coinage. But these states would have been obliged to make out of $15\frac{1}{2}$ lbs. of silver a quantity of coins the nominal value of which should correspond with that of 1 lb. weight of gold coins, and every one in the countries in question would have been obliged to accept the silver and gold coins as of exactly equal value. In this way the dealers, at the time when the ratio was 1 to 30, would have gained $14\frac{1}{2}$ lbs. weight of silver on every pound weight of gold they bought and then sold for silver which they proceeded to have coined. In more recent times as much as 37 lbs. weight of silver could be obtained for 1 lb. of gold. Hence if the various states had continued to coin the silver brought to their mints by private people, a man who exported 1 lb. weight of gold money and sold it for silver which he then brought back and had coined would have gained as much as 21 lbs. weight of silver. Under these conditions it is clear that not a single gold coin would be left in the countries which pursued such a policy.

By calculating the ratio of weights that have been mentioned into gold we get the following result. Until the year 1874, an ounce of silver cost about 60 pence in London, which has always ruled the market for the noble metals, and the price hardly varied from year to year; but at a later time an ounce of silver could be bought for about 21 pence; at present it costs 24 pence.

As the inhabitants of the German Empire have had a gold-standard since 1873, they are independent of fluctuations in

the price of silver. In countries which have a gold-standard gold is the only basis of currency. For that reason the law declares definitely that 200 marks are to be coined from one kilogram of silver, and that this coining is to be at the rate of 20 marks per head of the population, without regard to the price of uncoined silver. Therefore 20 marks in one-mark silver pieces are not of nearly the same intrinsic value as one 20-mark gold piece; for if these twenty coins were melted into a lump of silver, that lump, which would of course contain 100 grams of uncoined silver, would only be saleable by weight, and would fetch only a little more than 7 marks, as the present selling price of silver is about 72 marks per kilogram.

The action of the law has caused the twenty one-mark pieces to be worth much more than the silver in them was worth before coining; and at the same time the law lays it down that no one is obliged to accept more than 20 marks in silver in payment of a debt.* Silver money is therefore only subsidiary money.

It is certainly very remarkable that there should be throughout Europe a party, known as the bimetallists, who hope for the cure of all agricultural difficulties, or we may say for the better payment of all labour, and an increase in the value of every possession, by restoring, wherever possible, the ratio between the values of gold and silver to 1 to $15\frac{1}{2}$, and that this party should have been very eager at a recent time. The less violent partisans of this theory would be content, it is true, with establishing the ratio at 1 to 22 for the present—for the bimetallists are not unanimously agreed as to what they really want—while, as a matter of fact, the ratio keeps fluctuating around something like 1 to 37.

* Silver coins are legal tender up to 40 shillings in this country.—TR.

But it is just this fluctuation which makes any form of bimetallism impossible to-day. For if the various states should resolve, by an international agreement, once more to coin gold and silver money in a fixed ratio, say 22 lbs. weight of silver money for every pound of gold money, the effect of this would be to make silver more valuable, and so to cause the proprietors of silver mines throughout the world to increase the production of silver—the increase of which destroyed the old bimetallism, for that was in no way regarded by these silver owners while it existed—and this increased production would go on until an end should happily be made of the new international bimetallism.

Nothing could be done without an international agreement; for if a single state were to coin all the silver that might be brought to its mints into money at a ratio more favourable than the ratio of 1 of gold to 37 of silver, that state would be depleted, as we have already said, of all its gold coins in a few weeks.

Those countries, then, are best off which have a gold currency. The inhabitants of such countries have a stable standard of value, which is not subject to fluctuation, for all those things that can be compared in terms of gold, and for this reason all civilised states are in favour of a gold standard. Until about twenty years ago bimetallists disturbed people's minds by asserting that there was not nearly enough gold to make it possible for every country to have a gold standard, and that sufficient gold money could not be coined to supply the wants of commerce. But this trouble has disappeared, so far as the present generation is concerned at any rate, since the abundant finds of gold in South Africa, at Klondyke in North-Western America, and in West Australia.

There is one thing which the bimetallists would certainly achieve, as long as they do not get rid of the fluctuations in

the price of silver, were they to induce the civilised states to inaugurate an international bimetallism in that Utopia which they depict to any one who will hearken to them as the approaching economical rejuvenescence of the nations—for none of them has brought forward a decisive argument in favour of their assertions because no such argument exists, for if there were such an argument it would certainly quickly reconvert the most influential circles to bimetallism—and this one thing which they would undoubtedly do would be to enable the proprietors of American and Australian silver mines to make yet much greater profits from their mines, in which profits Europeans have as yet no great interests. Compared with these, the profits of the European silver producers could not be large because of the smallness of the European production.

All the other advantages which the bimetallists assert are to accrue to Europe by the adoption of their proposals rest on unproved ideas.

One cannot then be astonished that the supporters of bimetallism increased for a time after the subject began to address itself to the general public. Most of the frequenters of the meetings of bimetallists do not grasp as a whole the matters that are put before them because of the many difficulties of the subject; but still they are quite sure that restored bimetallism—that mystical word—will bring with it at least a part of the good fortune to which each one thinks he has an undoubted claim, and for that reason matters will then be different with them. Did not some of the troops who were at St. Petersburg in 1826 at the enthronement of the Tsar shout *Long live the Constitution* instead of *Long live Constantine*, because they had been told that the name of the new monarch was *Constitution*?

Independently of the use of silver for coinage, there is a

very large demand for that metal. The increasing luxury of the world is constantly demanding articles of silver; silver spoons, forks, silvered knives, and so on; the demand for the metal has not ceased with the cessation of the coining of sterling silver money; but the silver that is produced in the world no longer finds its chief employment in making coinage.

The base metals, to which we now proceed, are extracted from their ores, which are for the most part either oxides or compounds of the metals with sulphur. The process of extracting the metals from their oxides consists in heating the oxides mixed with coal or charcoal in suitable furnaces, whereby the oxide is said to be *reduced to metal.*

Oxide of iron + carbon = iron + carbon monoxide.

To convert the sulphur compounds into oxides, and so to obtain compounds from which the metals can be extracted on the large scale, it is necessary to roast the sulphides in the air; in this process the sulphur is burnt to sulphurous acid, and the metal to oxide, which is then reduced by heating with carbon. For example:

Sulphide of zinc + oxygen (from the air) = sulphurous acid + oxide of zinc
Zincblende.

and

Zinc oxide + carbon = zinc + carbon monoxide.

Were the sulphurous acid to escape into the air it would destroy all the plant life in the neighbourhood; it is therefore generally collected, nowadays, by the help of improved arrangements in the furnaces, and converted into

sulphuric acid. The equation just given represents the carbon as being burnt only to carbon monoxide when a metallic oxide is reduced to metal by heating with carbon, whereas in other cases we saw that it was burnt to carbonic acid. The reason for this is that the temperature required for the reduction of the metallic oxides is so high that at that temperature the carbon is able to bind to itself only a single atom of oxygen; the carbon monoxide that is formed in this way can at another time combine with a second atom of oxygen and thus be burnt to carbonic acid.

The following equations clearly present the changes:

Carbon + one atom of oxygen = carbon monoxide.
C + O = CO

Carbon monoxide + one atom of oxygen = carbonic acid.
CO + O = CO_2

Carbon monoxide is the intermediate stage of the burning of carbon to carbonic acid. We have gone into this matter with some fulness because we shall have to make use hereafter of this more accurate statement of what occurs in these processes.

We shall now make a more special study of the extraction of iron. Three sorts of iron have been distinguished for very many years.

Pig or *cast iron*, containing 2·3 per cent. or more than 2·3 per cent. of carbon;

Steel, which contains 1·6 per cent., or less than this, of carbon, but more carbon than the third variety;

Wrought iron, containing about half a per cent. of carbon.

Pig iron is relatively easily fusible, and can be cast, but not forged; steel can be worked in the forge, and the articles made in this way can then be tempered; wrought iron can also be forged, but not tempered afterwards. By *forging* is

meant the softening at a full red heat to such an extent that the iron can be worked by the hammer into any desired form. Both steel and wrought iron can be welded, that is, two pieces can be joined homogeneously by hammering at a white heat.

Many other kinds of iron are distinguished in the iron manufacture of to-day, but we shall discover that the preceding classification is sufficient for our purposes.

All commercial iron, then, contains carbon. While it is well known that endeavours are made to obtain all other metals as free from impurities as possible, because their peculiar properties are then most distinctly apparent, the case is different with iron. The contamination of iron with carbon, if such an expression may be used in this connection, is required in order to give to the iron those diverse properties which make it the most serviceable of all the metals.

Iron takes up more than 2·3 per cent. of carbon only at a very high temperature; hence pig or cast iron was quite unknown to the ancients. Wrought iron, however, has been known for ages. It is supposed to have been first made about 1500 B.C. by the Philistines. The production of this iron, however, depended on the degree of civilisation of a people, for it is told by Cæsar that when he came to Britain about 50 B.C. gold and iron were nearly equally valuable there, as the inhabitants possessed only those small quantities of the two metals which were brought to the country by traders. Methods of extracting iron were unknown at that time in England, which is the country where the most important discoveries in that direction were made at later times, and is also the country whose output of iron was for centuries greater than that of any other, although the output of England has been exceeded within recent years, not only by that of the United States of America, a country with an

area enormously greater than the area of England, but also by that of Germany.*

Enormous deposits of iron ore were discovered in America in 1890. In 1892, 4,245 tonnes (1,000 kilograms = 1 tonne) of ore, containing 58 per cent. of iron, were raised; in 1894, 17,921,705 tonnes; and in 1907, 28,000,000 tonnes were raised.

The extraction of iron cannot be made clear except we first realise the method and manner of the production of the high temperatures that are required in the processes; we must therefore approach the subject of the manufacture of iron from this side.

If wood or coal, or other combustible material, burns on the ground, only a flickering fire of little use as a source of heat is obtained, for the supply of air, which is needed for burning the carbon, is very limited. But matters are soon altered if the heating material is burnt on a support that is perforated so that the air can enter from beneath. We do

* About a hundred years ago, in 1807, the world's annual output of iron was 760,000 tonnes; it is now about 61,000,000 tonnes; this means that about 120,000 kilos. of crude iron are produced, and used, every minute of the year. The following figures give the output of pig-iron for each of the chief iron-producing countries, in the years 1882 and 1909:

	1882	1909
United States of America	4,600,000	27,636,687
Germany	3,400,000	14,793,325
Great Britain	8,600,000	10,380,212
France	2,000,000	4,032,459
Russia	400,000	2,740,000
Austria-Hungary	600,000	2,010,000
Belgium	700,000	1,803,500
Canada	—	752,053
Sweden	400,000	604,300
Spain	100,000	367,000
Italy	—	215,000
All other countries	500,000	525,000
	21,300,000	65,859,536

(A tonne = 1000 kilos. = ·9842 ton.)

this when we burn a fire in a grate; and if we also insure the speedy removal of the carbonic acid and the other products of combustion, by fixing an exit pipe at a proper distance above the fire, then the regular stream of air which flows into the fire brings about a uniformly rapid combustion of the materials in the grate. A pipe of this kind, which takes the form of a chimney in a dwelling house, acts as a means of producing a draught, for the carbonic acid formed in the burning and the nitrogen that comes in with the air, being much heated by the fire, become lighter, bulk for bulk, than the surrounding air, and therefore tend to ascend, and hence to cause a current inwards of fresh air to supply their place.

Many metallic oxides may be reduced in a fire of the kind described with the help of carbon, but oxide of iron cannot be reduced. This oxide is reduced only when the fire is saved the trouble of sucking in the air by blowing the air supply into the fire, whereby a very rapid combustion is of course produced. Every smithy fire is an arrangement of this kind wherein air is blown into the fire by the smith's bellows.

The ancients reduced oxide of iron in a smithy fire (see fig. 19). They sometimes obtained wrought iron and sometimes steel, for, according to the manner of working, sometimes less and sometimes more carbon entered into the iron, and it is upon the quantity of this constituent that the production of one or the other of these varieties of iron depends. The results were better or worse according to the purity of the iron ore used and the skill of the workmen who handed down the art from one generation to another. Hence came the great reputation of the blades of Damascus and Toledo, for instance; for the production of steel, which is a very

difficult art when only a smith's forge is available, had become a specialty of these districts and had been brought to great perfection.

Only those iron ores which are comparatively easily

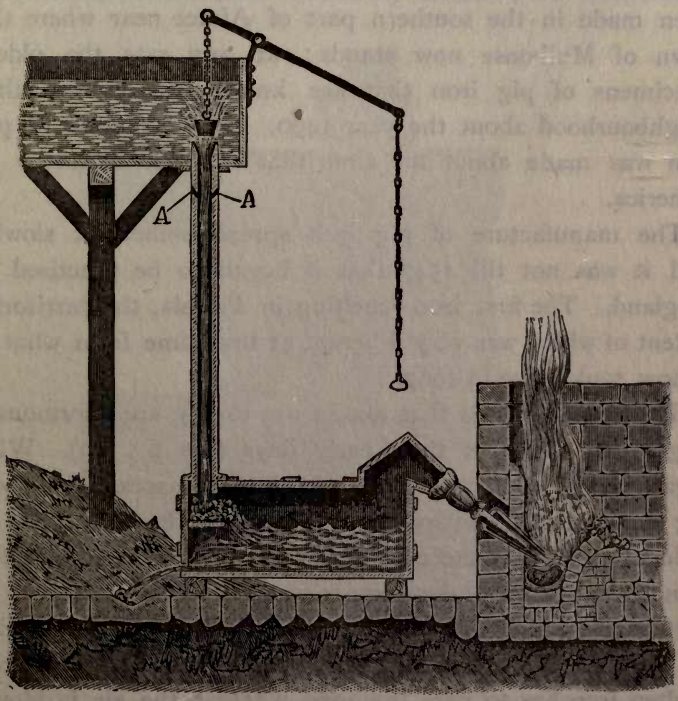


Fig. 19.

reduced can be worked in a smith's forge. But the production of iron spread gradually to different countries, and as easily reduced ores were not to be had everywhere, it became necessary to find means for increasing the heat of the furnace. This was done by building stones around the smithy fire and so converting it into a blast furnace. The

heat of the fire was not then lost in warming the surrounding air, but the stones became red hot and so concentrated the heat more in one place, and the temperature was raised so much that the reduced iron took up four, or more than four per cent. of carbon, and the pig iron thus produced ran from the furnace in a liquid state. This discovery seems to have been made in the southern part of Alsace near where the town of Mulhouse now stands; at any rate the oldest specimens of pig iron that are known came from that neighbourhood about the year 1490. The invention of pig iron was made about the time that saw the discovery of America.

The manufacture of pig iron spread somewhat slowly, and it was not till 1547 that it began to be practised in England. The first iron smelting in Prussia, the territorial extent of which was very different at that time from what it is now, took place in 1667.

The blast furnaces that are in use to-day are enormously larger than those of these early days (see fig. 20). With regard to the production of iron in these furnaces, the following points should be particularly noticed. The iron oxide is reduced to iron by the carbon (coal) in the furnace, and the iron sinks gradually downwards until it comes to a part of the furnace which is so hot that the iron takes up a quantity of carbon sufficient to cause it to melt; but after that, the molten iron has to pass the zone whereat the air is blown into the furnace, and at this place it would be again burnt to oxide of iron were not an especial precaution taken to prevent this. The formation of slag is the precautionary measure that is adopted.

Slag is a kind of glass; it consists of double silicates (see p. 200). Besides oxide of iron and coal, lime-stone and clay (the latter is a silicate of alumina), and when necessary sand

also, are thrown into the blast furnace. These things vary in different neighbourhoods and also in accordance with the constituents of the ores that are to be smelted, the most easily accessible and the cheapest substances that are suitable for the purpose being chosen. Those that have been mentioned are the most commonly used; at the temperature

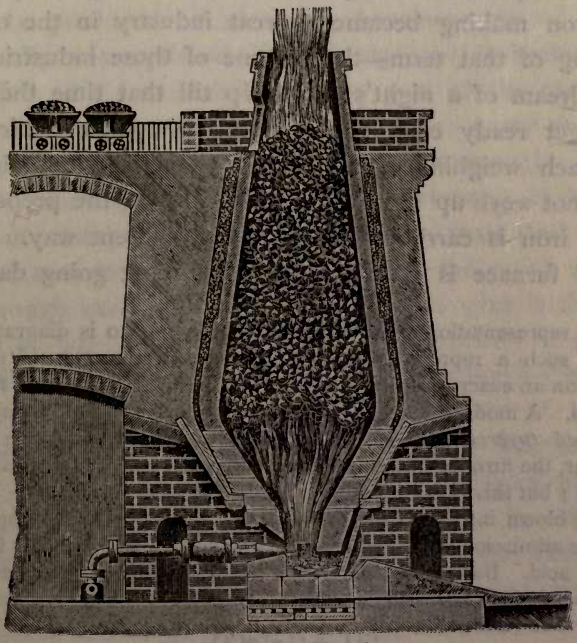


Fig. 20.—Blast furnace of 1830.

of the furnace they react to form a double silicate of lime and alumina, which is a kind of glass.

The mixture of the substances that are to produce the slag is always selected so that they run together to a glass only after the iron has taken up enough carbon to convert it into pig iron; this glass then covers the individual molten particles of iron and protects these from the effects of the air

blast. And in this way the iron passes the zone where the blast is sent in without being reburnt to oxide. Lower down in the furnace the heavy liquid iron separates from the lighter melted glass, and both flow out of the furnace as liquids.* When the iron solidifies it is called pig iron, and the solidified glass is called slag. (Slag is used for making cement, see p. 211.) It was only after the discovery of pig iron that iron making became a great industry in the modern meaning of that term—that is, one of those industries that never dream of a night's rest. Up till that time the smith could get ready each day two or perhaps three blocks of iron, each weighing about 80 lbs., and these he might or might not work up the following day. But the preparation of pig iron is carried on in quite a different way. When a blast furnace is started it must be kept going day and

* The representation of the blast furnace in fig. 20 is diagrammatic, because such a representation elucidates the preparation of pig iron better than an exact drawing of one of the monstrous modern furnaces would do. A modern furnace requires six or seven pipes for blowing in air [called *tuyères*], whereas only one is represented in the figure. Moreover, the furnace is shown open at the top whereat the flames are escaping ; but this is not the case in actual furnaces nowadays. The air which is blown into the furnace is heated to a very high temperature before its admission into the furnace. The carbon of the coal is burnt to carbonic acid. But this extremely hot gas reacts with the higher layers of hot coal to form carbon monoxide. Thus

$$CO_2 + C = 2CO.$$

Carbonic acid + carbon = carbon monoxide.

Hence carbon monoxide, which is an inflammable gas, escapes from the furnace, mixed with much nitrogen. In olden times this mixture, which contained from 24 to 34 per cent. of combustible gas, was allowed to burn at the mouth of the furnace, and so to be lost (as is shown in the figure) ; nowadays the furnace is closed by a hood, and the carbon monoxide is led from under this hood to places where it is burnt, and the heat is used for evaporating, or for heating the air to be sent into the furnace, or for other purposes of a similar kind. The gas from the blast furnaces is also used for driving gas engines.

night, else it would not get hot enough to melt any iron at all; but in return for this the furnace produces large quantities of pig iron, which has thus become a cheap commodity.

Pig or cast iron then contains more than 2·3 per cent. of carbon, and if it were possible to burn away a part of this carbon either steel or wrought iron (see page 253) would be produced. And such a burning away of carbon is actually accomplished. When pig iron is heated in a forge fire with free access of air a part of the carbon in the iron is burnt away, the mass becomes pasty and does not run to a liquid, and either steel or wrought iron is formed according to the skill of the workman. It is much easier and cheaper to make wrought iron than steel in this way, because it is very difficult to hit the point whereat just enough carbon is left in the iron to give it the properties of steel. But in making wrought iron it is only necessary to burn away as much of the carbon as possible, for enough always remains to give the whole of what is left the qualities of wrought iron. Now it was found to be so much easier to make wrought iron from pig iron than to manufacture it directly from the ores by the older process, which was the only method available before the discovery of pig iron, that the ancient method was soon abandoned, and as a consequence the manufacture of pig iron in the blast furnace has become the foundation of the whole iron industry.

This condition of affairs had been attained as early as 1620. The manufacture of pig iron had become a large concern in England by that time, as the conditions were more favourable in that country than elsewhere. The intelligence of the inhabitants eagerly turned to the best account the large quantities of iron ores that were raised

in that country, and the many rivers made it possible to transport the prepared iron without difficulty to other lands. The roads at that time, being badly constructed and easily disturbed by rains, were not adapted for the transport of great quantities of iron; hence the manufacture of iron could not be carried on profitably at any great distance from rivers or from the sea.

Wood charcoal was employed as fuel in the blast furnaces; but the great demand for wood led to the visible disappearance of the forests—independently of the destruction of forests, which was but little heeded in those days—and to the imperative necessity of finding some substitute for wood. Coal at once suggested itself. But a blast furnace cannot be worked with coal as the fuel; for before it burns, coal becomes pasty and tarry matter distils from it, and if coal were used in the blast furnace the single pieces would get glued together so that the air blast could not penetrate the mass, and the working of the furnace would be stopped.* The suggestion was made to change coal into coke—that is, to heat the coal in a closed vessel where it cannot burn for lack of air. All the volatile and fusible matters in the coal are driven out by this treatment, and a hard mass remains, which can be used as fuel in the blast furnace because it will burn without caking together. In making coke for use in the blast furnace no attention is paid to the volatile matter of the coal; it is only the residue—the coke—that is important (cf. pp. 28 to 30).

Coke began to be used in blast furnaces, in England, about the year 1700; and as it then became possible to obtain any desired quantity of fuel the production of cast iron went on

* Nevertheless, bituminous coal is used in blast furnaces in Scotland and North Staffordshire, and in parts of the United States.—TR.

increasing very considerably until about the beginning of last century, when that enormous advance began, the end of which we cannot yet see.

Coke is so hard that a blast furnace may be built about 30 metres [92 feet] high without the contents getting crushed and crumbled. In the olden days it would not have been possible to get the enormous quantities of raw material which such a furnace requires into the furnace; and it was only after the invention of steam engines and railways that it became possible to feed furnaces of such a size.

A blast furnace using charcoal as fuel, such as may be found at work to-day in Styria, could turn out daily, about the year 1800, from 3,000 to 4,000 kilograms [nearly three to four tons] of cast iron; but a very large modern blast furnace, using coke, produces daily nearly 600,000 kilograms [about 590 tons] of the same substance.

The modern blast furnace is not built of stone, but almost wholly of plates of wrought iron, or steel, which are covered on the inside with a layer, some 4 inches thick, of fire-resisting stone. The iron plates must be continually cooled; about 6 litres of cold water are required per minute to cool each square metre of surface [about one gallon of water per minute for each square yard of surface]. In 1880, about 8 tonnes of coke were used for each tonne of pig iron produced; in 1850, only about 3 tonnes of coke were used; and in 1900, about 1 tonne of coke was required, which is about the minimum quantity theoretically possible. The immense importance of iron in the scientific life of peoples is made clear by the fact that the money value of the iron produced in the year 1900, although iron is the cheapest of all metals, was one and a half times greater than the value of all the other metals taken together, including gold and silver.

While the mechanical parts of the operation of iron smelting were being brought to perfection, chemistry was busily engaged in trying to elucidate the processes that occur in the blast furnace, for these processes are certainly not so simple as we have represented them in the sketch that has been given. And since it has become perfectly clear that the properties of different kinds of iron are conditioned by the percentage quantity of carbon which each contains—a statement that is far from being self-evident—advance has ceased to be slow; and indeed such rapid progress has been made on the basis of this knowledge that the present generation may be said to be passing from the age of iron to the age of steel.

The remark has already been made that scarcity of charcoal led in England to the erection of blast furnaces which should use coke as their fuel. All the pig iron obtained by the use of these furnaces, except what is employed for making articles of cast iron, was, and is, manufactured into steel or into wrought iron. The preparation of wrought iron was carried on in small furnaces with strong air draughts, wherein the carbon was gradually burnt away until only about ½ per cent. remained; the product was wrought iron. It was necessary to use charcoal for this purpose, because the ashes of coal or coke contain substances which react chemically with the iron while it is being worked up with the fuel in such a way that the wrought iron produced is quite useless.

While it was possible many years ago to obtain pig iron, produced in large works, in quantity and at a low price, wrought iron long remained as expensive as it had ever been, for it was still made on a small scale, and each lump of iron was worked on the hearth of a furnace, just as used to be done in olden days; and in addition to

this, charcoal, which is an expensive fuel, was used in making it.

But a revolution was brought about by the discovery made by Cort, an Englishman, and patented by him in the year 1784. Cort hit on the plan of separating the fire from the pig iron in making wrought iron ; as the ashes of the combustible material were thus prevented from coming into contact with the iron these ashes had no influence on the product. He carried on the making of wrought iron in a reverberatory furnace ; and his process, which is called

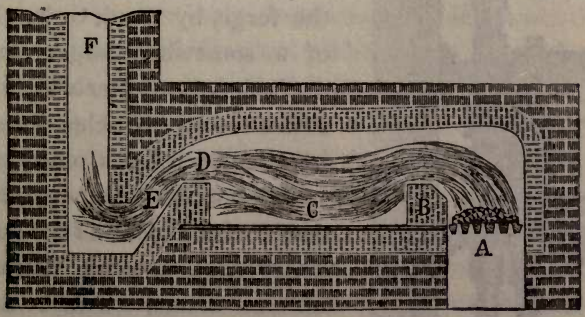


Fig. 21.—*A*, Grate, whereon the fuel is burnt. *B*, Fire bridge. *C*, Furnace bed, whereon the iron is heated. *D*, Flue bridge. *E*, Flue. *F*, Chimney.

"puddling," has remained in use until now, although changes, to which we shall refer immediately, have been made in the arrangement of the furnace. In a reverberatory furnace it is only the flame of the burning fuel that plays on the iron (see fig. 21). The iron does not come into contact with the ashes of the fuel.

This process is capable of manufacturing large quantities of wrought iron, inasmuch as a great many pigs of iron may be placed at the same time on the bed of the furnace, which is separated from the fuel by the fire bridge, and the carbon of these pigs will be gradually burnt away until only a very

little is left; and as the furnaces must be kept working uninterruptedly day and night, that the proper temperature may be maintained, the manufacture of wrought iron has become one of those industries that are conducted on a very large scale.

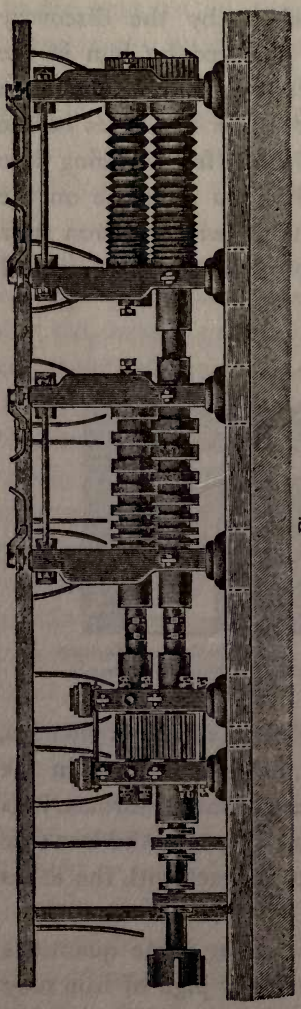


Fig. 22.

Previous to the improvement made by Cort it had been customary to hammer out each lump of iron, as it was made in the forge, by hand, or by the use of a somewhat larger hammer worked by a water-wheel. The surfaces of the articles of wrought iron made by this older process were never quite smooth, and the marks of the blows of the hammer could be seen upon them, even on iron bands, which to-day are made as smooth as if they had been polished.

The masses of wrought iron produced by the older methods of puddling were not at all amenable to further treatment. Cort introduced the rolling of wrought iron. He shaped the pieces of iron that left the furnace into the desired forms by squeezing them while red hot between rollers (see fig. 22). If the two rollers work close on one another, and corresponding

pieces are cut out of the upper and under rollers, band or square iron is obtained, and if the indentations are truly cut the bands must come out of the rolling mill with perfectly smooth surfaces. If a cutting the shape of the top of a railway rail is made in the upper roller, and one which has the form of the lower part of such a rail is made in the under roller, then the rolling mill turns out rails. A sheet of iron is obtained by passing a piece of iron between two smooth rollers fixed at a convenient distance from one another; and so on.

Like many other great inventors, Cort derived no material advantages from his ideas and labours which have done so much to advance civilisation. The many researches that were needed to bring his ideas into practicable shape swallowed up his means, and he died in poverty.

James Watt had invented the steam engine towards the end of the eighteenth century. But the work which the engine could do was very limited, because the steam that was needed to keep it going could be produced only in cast-iron boilers, and no one at that time knew how to make these of considerable size. This was not changed until the process of rolling iron made it possible to manufacture large uniform plates of wrought iron. Large boilers can evidently be made by riveting such plates together,* and such quantities of steam can be produced in these boilers as suffice to set in motion the largest machines.

Attempts began to be made in the early years of last century to employ steam engines in place of horses for traction purposes.

As has been mentioned, most of the English mines are situated near rivers, and it was long ago customary to lay down wooden tracks for the easier conveyance of heavy

* Steel plates are used nowadays.

loads from the mines to the rivers; sleepers were placed on the ground, and then joined into a continuous track by long pieces of wood. In order to do away with the need of frequently renewing the long pieces of wood between which the horses walked the custom was to lay boards over these, so that when the boards were worn out by the passage of the wheels over them they could be replaced by others.

In the year 1767 the iron industry was affected by an extraordinary crisis, which became so severe that at last cast iron was quite unsaleable. A large ironworks that had a considerable stock of pig iron cast a part of its stock into oblong plates, that the iron might not be lying altogether useless, and laid these down on the foundations of a wooden tramway in place of the boards that had been used before; this road thus became the first *railway*, as we call such a construction nowadays.

The experiment turned out a great success. The horses were able to draw much heavier loads on this smooth support than on the boards that were formerly used, and the wear and tear of the iron was extremely small. When the crisis in the iron trade was over, not only did this railway remain, but all the other works gradually adopted the new contrivance.

Here, then, in the literal meaning of the word, was laid the foundation for steam carriages. Stephenson had about that time constructed the first locomotive that was of practical use for the conveyance of human beings.

An examination of the English patent literature of that period shows what a vast number of proposals was made, and how many investigations were undertaken, with regard to steam carriages, all of which came to nothing; and it also makes one better appreciate the esteem in which his contemporaries held the discoverer who at last hit upon the true

solution of an extremely difficult problem which had been attacked by so many others.

After the invention of the process of puddling it was easy to obtain both cast and wrought iron ; but circumstances still remained very unfavourable to the production of steel, which is the most valuable form of iron so far as usefulness is concerned.

It is just as difficult to make steel from pig iron by puddling as it used to be to make wrought iron by the old forge method. There is no theoretical objection to the method, for all that need be done is to stop the puddling when the iron contains just enough carbon to form steel ; nevertheless this can scarcely be done in practice.

As long ago as the beginning of the eighteenth century, that is, long before the invention of puddling, a new method of preparing steel was found out in Northern France; the steel made by that method was known as *cementation steel.* The earliest truly scientific work on this subject was carried out by Réaumur, who lived at that time, and whose name is generally known in connection with the thermometric scale which he introduced.

If sufficient carbon could be added to wrought iron to bring up the quantity of carbon from $\frac{1}{2}$ to about $1\frac{1}{2}$ per cent., then, in accordance with the sketch given on p. 253 of the different kinds of iron, we should expect that steel would be produced. The preparation of cementation steel depends on this principle. The wrought iron is cut into bars, and these are packed in charcoal powder in fireclay chests capable of containing about 8,000 kilos (say 8 tons), set in a convenient manner in a furnace which is kept heated to about 1,000° C. (about 1,800° F.) for a period of six to eight days. Under these conditions a gradual permeation of the iron by the

carbon takes place, and the iron is changed completely into steel.

Steel made in this way cannot be quite homogeneous, for the outer parts of the bars will be richer in carbon than the inner portions. A remedy for this was sought in the vigorous working of the steel under the hammer.

In 1730 an English watchmaker called Huntsman discovered a perfectly homogeneous steel that cannot be surpassed to-day. He found, as every one else did, that very many of the watch springs he worked with snapped, because of the unequal character of the steel of which they were made, and in attempting to remedy this he discovered that small quantities of cementation steel could be melted in crucibles placed in an extremely hot furnace.

This can be easily understood by us; we know that iron containing 2·3 per cent. of carbon melts comparatively readily, and there seems to be no reason why iron containing less carbon should not also melt if a sufficiently high temperature were attained.

The cast steel discovered by Huntsman is perfectly homogeneous throughout, and, as the hardness of steel is not diminished by melting, this cast steel is a material that cannot be replaced for many purposes by anything else. The method of manufacture remained a secret with certain English makers, who asked fancy prices for their steel; and these prices were paid because a material equally suitable for many purposes could not be obtained anywhere else. Many efforts were of course made to find out the method whereby this English steel was secretly manufactured. The founder of the Krupp iron works was one of the most determined workers in this direction, and although he did not live to see the problem solved completely, his son succeeded in producing such perfect cast steel that Krupp's

works became the largest iron manufactory in the world. These works employed 66,300 workmen in 1909; in 1910 the American Steel Trust employed, in all its departments, about 205,000 workpeople.

Cast steel of this kind (called *crucible steel*) leaves nothing to be desired, but it must always be expensive because of the great number of processes required in its preparation; for pig iron must first of all be made into wrought iron, and this must then be caused to combine with carbon, and finally the steel must be melted in crucibles in an extremely hot furnace.

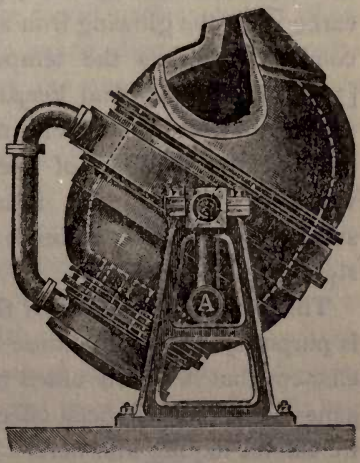


Fig. 23.

Bessemer was the first to supply the world with cheap steel very nearly identical with crucible steel. In a lecture delivered at Cheltenham on August 13th, 1856, he made the astonishing announcement that steel, which was costing from 1,000 to 1,200 marks per 1,000 kilos (£50 to £60 per ton), could be produced for from 120 to 140 marks (£6 to £7 per ton). Bessemer's process converts molten pig iron into cast steel "without the consumption of fuel." While a puddling furnace changes about 3,000 kilos of pig iron into wrought iron in twenty-four hours with the expenditure of much coal, the Bessemer process effects the same change of pig iron to wrought iron, and to steel, in fifteen minutes.

For this purpose Bessemer brings the melted pig iron into a pear-shaped vessel, provided at the bottom with a row of pipes for blowing in air (see fig. 23). The vessel [which

is called a "converter"] is constructed of iron plates riveted together, and to enable it to resist the high temperature attained in the process it is lined with an extremely fire-resisting material, which for long consisted almost wholly of silicic acid.

The converter is inclined horizontally [it rotates on trunnions fixed on both sides somewhat lower than the middle of the vessel] and the melted pig iron is run into it, and while it is being brought into the vertical position air is blown in through the pipes in the bottom. The red-hot carbon * in the glowing iron at once begins to burn, and this combustion raises the temperature to 1800° or 2000° C. [3300° to 3600° F.] and keeps the contents of the converter melted. After about ten minutes the carbon is all burnt off, and the contents of the converter would be valueless were not sufficient pig iron added, at this moment, to supply just enough carbon to convert the whole mixture into steel.

The iron that is added for the purpose of supplying carbon is purposely selected because of its richness in *manganese*, an element that is closely allied to iron, for the presence of manganese exerts a beneficial effect on the product in a way that we cannot inquire into here. The word *spiegeleisen* † is often met with; it is the especial name for a kind of pig iron that contains manganese and shows a lustrous surface when broken.

Manganese is manufactured in some of the metal smelting works to-day for the purpose of being used in the Bessemer

* And also the *silicon* which gets into the iron in the processes that occur in the blast furnace; for at the high temperature of that furnace a little silicic acid, which consists of silicon and oxygen, is reduced to silicon, which dissolves in the iron.

† *Sparkling iron*; the German term is generally used in English books.—TR.

process, for this metal taken alone has not as yet found any industrial applications.

The Bessemer process enables steel to be manufactured on a very large scale, for a single converter will contain from 10,000 to 16,000 kilograms [approximately 10 to 16 tons] of pig iron, and the whole of this is converted into steel in a quarter of an hour.

Before leaving the Bessemer process we must say a little regarding the dephosphorising of iron, a process which should further cheapen the cost of steel.

Most of the iron ores that are found native contain phosphorus. The pig iron that is made from such ores also contains phosphorus, and unless the quantity of phosphorus is extremely small this iron is of a poor quality, and is only fitted for making the coarsest sorts of cast-iron ware in which no great durability is looked for; such pig iron could not possibly be worked up into wrought iron or steel. The analyses of pig iron made between 1830 and 1840 showed that the unsuitability of certain pig irons for making steel or wrought iron was connected with the presence of phosphorus in them. At that time no method was known for keeping the phosphorus contained in the ores out of the pig iron during the processes that go on in the blast furnace; nor has any method yet been discovered.

Notwithstanding the almost constant attempts to dephosphorise iron no result worthy of mention was obtained until Thomas and Gilchrist finally solved the problem in the most ingenious way.

Many investigations had proved that the original Bessemer process did not remove a trace of phosphorus from the iron used. All the phosphorus in the pig iron employed remains in the steel that is produced, and therefore in the rails, or the axles, or the surgical instruments, etc., made of that steel.

As regards rails, one-tenth, or at the outside two-tenths, of a per cent. of phosphorus might be permitted; but for all other applications of steel the presence of even the tenth of that quality is quite out of the question.

The raw material suitable for the old Bessemer process, which is dependent on the use of iron ores free from phosphorus, is found, as far as European interests are concerned, only in the red iron ores, containing no phosphorus, which occur in Cumberland and Westmoreland, in Spain, Algeria, Sweden, Styria, and in the district around Siegen.

An immense sensation was produced among those connected with the iron industry by the announcement, in 1879, that pig iron containing phosphorus had been converted into steel free from phosphorus in the Bessemer converters of Bolckow, Vaughan & Co., the largest ironworks of the Cleveland district.

Before the discovery of the Bessemer process the rails that were manufactured for railways were made of wrought iron, because steel rails could not be procured easily; but this was completely changed by that discovery. Because of their much greater durability, the steel rails that are turned out so cheaply by the Bessemer process have completely taken the place of the iron rails that were formerly used.

A large steel rail industry sprang up in Cumberland, but this industry did not flourish in Cleveland, where the iron ores are unsuited for making this kind of steel because of the phosphorus they contain. And the manufacture of wrought iron rails which had been carried on in places where the local ores contained very small quantities of phosphorus, had to be abandoned, because the use of such rails was being gradually dropped by the railway companies, who were more and more favouring the employment of steel rails.

The Cleveland manufacturers then determined that they also would manufacture steel rails, and that they would turn their great appliances to the best account by making use of Spanish ores which contained no phosphorus. So they manufactured pig iron for making Bessemer steel from these ores, and their undertaking was crowned with success.

But the Cleveland iron masters were not satisfied ; they set themselves with determination to solve the problem of finding a method which would allow them to use in the Bessemer process the iron ores that were so plentiful in their district, which were indeed almost lying at their door. And the technical chemists, Thomas and Gilchrist, whose names have been mentioned before, succeeded at last in the following way.

We laid stress on the fact that in order to make his converter withstand the action of heat, Bessemer lined it with a very fire-resisting material which contained much silicic acid, and which in a chemical sense was therefore acid. Thomas and Gilchrist, on the other hand, lined the converter with a basic lining which contained much lime.

At the high temperature which is attained in the converter the carbon of the pig iron is burnt, as we have seen ; and, as we should expect, the phosphorus is also burnt, and burnt to phosphoric acid. But whereas in the original process this phosphoric acid remained in the molten mass, in the modified process it is able to combine with the basic lining, it enters into union with the lime and forms phosphate of lime. And so the problem of dephosphorising iron in the Bessemer converter was solved. The pig iron that contained phosphorus yields steel that is free from phosphorus, because the phosphorus is held fast, as phosphoric acid, by the basic lining.

When the phosphate of lime formed in the linings is finely ground it forms what is known as Thomas's phosphate

powder, and is used by farmers for manuring meadow land (see p. 45). And thus it is that the phosphorus which was formerly so harmful becomes saleable in this form, and so bears its part in reducing the cost of steel. The fact that iron ores containing phosphorus are cheaper, because they are obtainable all over the world, than those that are free from phosphorus, also tends in the direction of cheapening steel.

It must not be supposed, as might perhaps be imagined from what has been said, that the process of these fortunate inventors fell into their hands from the skies. On the contrary, it was the fruit of year-long labours and at least a decade of arduous exertion. The preparation of a sufficiently fire-resisting basic lining for the converter alone consumed the labour of many years and a large expenditure of money before it was possible to be certain that the considerations which had led to the choice of this material would prove themselves workable on the large scale.

Inasmuch as most epoch-making discoveries are the products of many years of toil, and are not as a rule isolated brilliant ideas, it often happens that disputes about priority arise after these discoveries become known. Thus we find that the idea of using a basic lining in the Bessemer converter for the purpose of removing phosphorus was suggested in the literature pertinent to these subjects in various countries in 1875 and again in 1878. But it seems to have been regarded as an impracticable undertaking; yet the question was solved in 1879 in this very way in England.

There is another ancient method for changing pig iron into wrought iron. It is a difficult, and therefore expensive process to make of wrought iron such objects as the angle-pieces and T-pieces that are required for leading gas into living rooms, keys, door- and window-fastenings, and so on. Such

small objects are made of pig iron, and are then packed between layers of iron oxide (natural iron-ore is used) in fire-resisting boxes, in which they are heated for from ten to twenty days. The oxygen of the iron oxide reacts with the carbon in the pig iron, and burns it away. When the objects are taken out of the boxes they contain so little carbon that they have the properties of wrought iron; they can be worked as wrought iron is worked.

Another and quite different method for making steel may be supposed possible. Pig iron contains more than 2·3 per cent. of carbon, and wrought iron contains about ½ per cent.; if a mixture of these two in the proper proportions were melted, a mean product which would have the composition of steel would be obtained.

The difficulty that for a long time prevented the carrying of this idea into practice was that no reverberatory furnace could be constructed to give a sufficiently high temperature to effect the solution of wrought iron, which is infusible in an open furnace, in molten pig iron so as to produce steel.

The French manufacturer, Martin, was the first to produce this *soft steel*; but Siemens had constructed furnaces in 1885 wherein such steel could easily be prepared.

In speaking of puddling, we mentioned that that process had remained essentially unchanged since Cort's discovery, except as regards methods of heating the furnaces. Only those very good, and therefore expensive, sorts of coal which burn with a long flame could be used in the puddling furnaces, as it was necessary that the heat should be obtained from the flames which shot out from the grate over the fire bridge. But nowadays the heating is done by gas, which is produced on the spot from what are called *generators*.

For the purpose of heating by gas, fuel, which need not be of first-rate quality, is shot from a height on to a grate. Under these conditions the quantity of air in contact with the fuel is not sufficient to burn the carbon completely to carbonic acid, and therefore carbon monoxide and other combustible gases escape from the generator.* It must be noticed that the whole of the nitrogen in the air that enters the furnace through the grate is found in the gases which escape from the generator.

The chief difference between such generator-gas and ordinary coal-gas, the latter of which is obtained by heating coal in closed retorts (see p. 28), is that the coal-gas does not contain nitrogen and consists only of combustible gaseous substances.

The hot gases which come from the generator are burnt in reverberatory furnaces into which air is conducted. The gases pass through passages in the walls of the generator whereby they are heated.

Mond has introduced generators for using the poorer sorts of bituminous coal. Steam is passed continuously through the generators, whereby a very cheap gas is obtained, which is useful as a source of power in many industries. These generators made it possible, in 1909, to solve the problem of using peat for technical purposes. Peat containing from 45 to 60 per cent. of water can be converted directly into heating gas in these generators, and the simultaneous recovery of the nitrogen of the peat in the form of ammonia serves to reduce the cost of the gas. The enormous quantities of peat in various countries may now be advantageously used. All former attempts to use peat on a large scale involved the removal of the water from the peat before using it as a com-

* The reactions have been more thoroughly described in the note on p. 260.

bustible material, and this preliminary treatment made the processes uneconomical.

The most important improvement in turning to the best advantage the gases made in generators consists in the use of the *regenerators* introduced by Siemens. When the gas had done its work in gas furnaces, that is, had heated the substances to be heated, the hot mixture of the products of combustion used to be allowed to escape by the chimney. But the regenerators retain the heat of the burnt gas. For this end, the burnt gas, which seems to have fulfilled its special purpose, is led through chambers which are built with cross-bars made of fireclay bricks, and it is not until it has given up its heat to these chambers, which are thereby raised to a full red heat, that it is allowed to escape by the chimney. These red-hot chambers form the regenerator. When the gas leaves the generator in which it has been produced it passes through the red-hot chambers of the regenerator, and is thus made very hot, and it is then allowed to come into the reverberatory furnace, where it meets with sufficient air to burn it. The air also is passed through a red-hot regenerator before it enters the furnace, and carries with it into the furnace the heat which it has taken up in its passage.

As the chambers of the regenerator can be connected and disconnected by means of valves, they can be heated in turns so that red-hot chambers are always ready for heating both the gases and the air, and as soon as these chambers have given up their heat they can be heated again. The saving of fuel effected by this method, as compared with the old processes, amounts to from 40 to 50 per cent. In the year 1895 Siemens made further improvements, which increased the efficiency of the regenerators. All the burnt gas escaped

through the chimney; that is to say, all the carbon in the gas passed away as carbonic acid. Siemens made the completely burnt hot gas, mixed with the air which made possible the combustion in the generators, pass again through the generators, where it came into contact with burning coal, wherewith it reacted to give combustible carbon-monoxide, which afterwards could be used in the furnace for obtaining high temperatures.

Notwithstanding the application of generators and regenerators to reverberatory furnaces, it was still impossible to manufacture soft steel or soft iron (for these are the names given to the steel produced by melting together wrought and pig iron) in such furnaces. The *open flame furnaces* invented by Siemens made this possible for the first time. From theoretical considerations on the nature of flame, Siemens came to the conclusion that if the full heating effect of a flame is to be obtained the flame ought not to play on the walls of a furnace, but must burn in the reverberatory furnace itself in the form of an enormous tongue. Until the year 1885 the flame was arranged so that it filled the furnace as nearly as might be; but the size of the flame has now been increased, and the success attained has been very remarkable. The temperature of the furnaces has been raised to such a height that the best fireclay bricks can scarcely resist it, and soft steel or soft iron can be produced with comparative ease.

In working the Siemens-Martin process, the furnaces were at first lined with material which was acid in the chemical sense. At a later time a basic lining was used, and raw material containing phosphorus was dephosphorised in the process. Since 1899 the process has been made continuous. For a time it seemed that the Thomas process and the basic Siemens-Martin process would be dangerous competitors

against one another in the manufacture of the two kinds of soft iron. But this anticipation has been disproved; the two processes act as supplementary to each other; the question of which soft iron is to be preferred is determined by the special purposes of the user. The soft iron produced by the basic Siemens-Martin process is so excellent, so easily worked, that it has become a very dangerous competitor against wrought-iron produced by the ordinary puddling process. For making the soft iron, old pig iron and old wrought iron can be melted together; hence the Siemens-Martin soft iron is produced very cheaply. The more expensive iron made by puddling may be driven out of the market by the newer process. In Upper Silesia puddling has almost ceased since 1910.

We have now become acquainted with the development of the iron industry up to the present time. Something will be said in the next lecture about the production of steel in electric furnaces.

The methods of extracting such other metals as copper, lead, nickel, etc., reduce themselves finally to converting the naturally occurring ores into oxides and reducing these by means of carbon. *Zinc* and *aluminium* are the only two common metals not obtained in this way which we need speak of.

Their beautifully variegated copper roofs form part of the ornamentation of many old buildings, such as churches and castles. When we wish to cover spaces nowadays with metal plates—and this is done much more than it used to be—we almost always employ sheets of zinc, which are used chiefly because they are so much cheaper than copper, although it must be admitted that after a time they acquire an unpleasing

grey colour. As it is only about a hundred years since the art of making zinc plates arose, it was impossible to use zinc as a covering material in the olden days.

The reason why metallic zinc has been manufactured only in recent times is as follows. If a mixture of oxide of zinc and carbon is heated, reduction certainly takes place with the formation of zinc and carbon monoxide, but the temperature whereat this reaction occurs is so high that the zinc, which is a comparatively easily volatilised metal, is vaporised. If zinc oxide is heated with carbon in one of the furnaces that were formerly used for reducing metals, vapour of zinc is soon given off, but at the temperature attained this is at once burnt to oxide, so that no metallic zinc is obtained by this method of working.

It was about the middle of the eighteenth century that the extraction of zinc began in Europe—the Chinese seem to have practised the art at an earlier time—by heating zinc oxide and carbon, not in an open furnace, but in a retort, that is to say, in a closed vessel, by means of a fire applied outside the vessel. The zinc vapour could not burn under such conditions, and the zinc was obtained in the form of metal which distilled from the retorts. It was not, however, until the beginning of the last century that the method of making zinc plates from the very brittle metal obtained in the way described was discovered. These zinc plates are employed nowadays for all sorts of purposes, and the discovery of a means of making them has caused the zinc industry to assume very large dimensions.

The properties of aluminium, the metal most recently introduced into daily life, are very different from the properties of those metals we have spoken of hitherto.

Aluminium is the most widely distributed of all metals, and is found in the largest quantities over the earth. The

oxygen compound, the oxide, of this metal has long been called *alumina* by chemists. The name aluminium is connected with *alum* (Latin, *alumen*); alum has long been known to be a compound of alumina, namely a double sulphate of potash and alumina (see p. 140).

We also know that all the clays are silicates of alumina (see p. 212). Every brick is rich in this metal, and every potsherd would be the raw material—the ore—from which the metal might be obtained, were alumina reducible by carbon in the way that many other metallic oxides are reduced. But this is not the case, for that method is altogether barred in this instance, because the avidity of oxygen for aluminium is greater than for carbon, and carbon, therefore, cannot decompose oxide of aluminium.

The reduction of their oxides is not the only method whereby metals can be prepared in the laboratory. There are other methods, some of which are very complicated, and it was by one of these that aluminium was first procured in 1827. Attempts have been made uninterruptedly since the beginning of the fifties of last century to apply some of the laboratory methods on the large scale.

The first experiments which were conducted with large quantities of material were put on foot by Napoleon III. It was the time of the Crimean war, and he hoped to be able to use the very light metal as armour for the soldiers. These investigations led to improvements; nevertheless aluminium prepared by these processes, which employed only purely chemical methods, would have remained difficult to obtain and very costly. The invention of dynamos suddenly made it possible to obtain very large quantities of an agent that had been used for long in the laboratory in the production of metals, but had been very expensive until about that time; this agent was electricity.

Until the introduction of dynamos, the electricity used for technical purposes was obtained from galvanic batteries, the working of which was costly. Electricity was used in the metal industries for one purpose only, for the coating of cheaper with more expensive metals. This process, discovered in 1839, is called *electro-plating*. Large quantities of silvered goods have been prepared by this process since the middle of last century. The process is applied to-day on a large scale to depositing nickel on other metals; nickel so resists the action of air and water that it retains its lustre for an indefinite time.

We should say a word about the historical development of the subject. The action of electricity on chemical compounds was investigated many years ago. Priestley, in 1775, announced that the fire (for that was the name used in those days) produced by frictional electricity decomposed ammonia gas. We know that ammonia is a compound of nitrogen and hydrogen (see p. 29); if electric sparks are allowed to pass through that gas a mixture of nitrogen and hydrogen is produced, after a time, in place of the ammonia. No one at that time could have imagined that after about a hundred and twenty years this observation would place a new metal, aluminium, at the disposal of mankind.

In 1782 the discovery was made that the electric fire could decompose water into its constituents hydrogen and oxygen, and in 1800 it was ascertained that not only frictional electricity, but also the galvanic current, which had been discovered ten years before that time, could do this.

As it was not very difficult to obtain electric currents by the use of batteries, the action of the current on chemical compounds was further investigated, and in 1806 the extraordinarily light metal *potassium*, and soon afterwards also

the metal *sodium*, were obtained by *electrolysis* of compounds of these metals.

And in this way chemists became acquainted with two quite new metals, which are not only lighter than water, but have such affinity for oxygen that they burn when they are thrown on to water; they do this by eagerly withdrawing oxygen from the water and combining with it, and the heat produced in this process is so great that the hydrogen, which is set free from the water, takes fire in the air and causes the metal to burn also.

There seems to be no practical application for these metals, potassium and sodium, in ordinary life. But it is otherwise with aluminium, with which we are specially concerned at present; for although aluminium is a very light metal, and is obtained only by means of electricity, yet it is quite unchanged when exposed to water or the air, and therefore is of great practical utility.

The preparation of aluminium was accomplished by the aid of electricity in the following way, after a quite incredible number of attempts that ended in failure. Alumina is thrown into a melted mixture of cryolite (see p. 209) and fluorspar, and an electric current is passed into the fluid mass (see figure of electric furnace, p. 35); the current decomposes the alumina into its constituents aluminium and oxygen; the aluminium melts and collects at the bottom of the furnace, and the oxygen gas passes away.

In 1855, 1 kilo. of aluminium cost 1,000 marks; in 1856, 300 marks; in 1886, 100 marks; and in 1910, 1½ marks. In the year 1910, 50,000 tons of aluminium were produced. [The cost fell from about £25 per lb. in 1855 to about 8*d.* per lb. in 1910.]

The expectations that aluminium would find many uses have not been completely realised. When the metal became

cheap most of the many articles of daily use that were made of it at one time were forgotten. Neither aluminium nor alloys of this metal are applicable to ship-building, because they do not withstand the corrosive action of sea-water. Aluminium is used for making vessels for chemical factories and breweries; and its use for making cooking vessels is increasing. The difficulty of soldering aluminium has been overcome, as it was shown, in 1907, that pieces of this metal can be joined by autogenous soldering (see p. 35). Aluminium is an increasingly serious competitor against copper.

LECTURE XII

ALLOYS: Coinage—Bronze—Patina—Brass—Tombac—Talmi gold—Nickel silver—Britannia metal—Type metal—Nickel steel—Rare metals.

ALKALOIDS: Methane—Acetylene gas—Benzene—Pyridine—Coniine—Quinoline—Kairine—Antipyrin—Phenacetin—Narcotine—Chloral—Ether—Hoffman's drops—Chloroform—Antiseptics—Iodoform—Carbolic acid—Corrosive sublimate—Salicylic acid.

METALS are used not only by themselves, but *alloys* are formed by melting together several metals, and the properties of some of these alloys render them more valuable for certain purposes than their single constituents. For instance, those particular metallic alloys which are used for making coins pass through our hands every day. Pure gold, like pure silver, is so comparatively soft that both would wear away too quickly in commercial transactions. Older coins would soon fall off in their metallic value compared with those newly coined. But this happens only to a very small extent with the coins that are now used, inasmuch as copper is mixed both with the gold and the silver employed for coinage, for experience has shown that a sufficiently hard alloy is thus produced. The alloy of which German gold coins are made consists of 900 parts of gold and 100 parts of copper melted together. As 0·3584 gram of gold forms the coinage unit, under the name of *a mark*, a 10-mark piece weighs 3·982 grams (3·584 grams gold + 0·398 gram copper). German

silver coinage is made from an alloy of 900 parts of silver and 100 parts of copper, and 200 marks are coined from 1 kilogram of silver. No heed is taken of the intrinsic value of the silver, nor of the fluctuations in this value, for gold is the standard. One kilogram of silver is at present worth about 72 marks. The German nickel coins are struck from an alloy of 1 part of nickel with 3 parts of copper, and in a 10-pfenning piece there are 1 gram of nickel and 3 grams of copper. The German bronze coinage alloy consists of 95 parts of copper, 4 parts of tin, and 1 part of zinc, and 300 2-pfenning pieces or 500 1-pfenning pieces weigh 1 kilogram.*

The mention of the bronze coinage leads naturally to the consideration of bronze and brass.

Bronze† is a mixture of copper and tin in which the copper always preponderates. It is the most ancient of all known mixtures of metals. Most investigators are of opinion that all the metallic utensils that men used before the discovery of a method for extracting iron were made of bronze; hence it is customary to speak of *the bronze period*, which certain people think was preceded by a period of copper.

Bronze is still manufactured in very large quantities, and it is employed for all sorts of purposes. Not only as church bells does it send its warning sound to the ears of the solitary man, but also in the form of cannon, which only began to be

* The English gold coinage alloy consists of 11 parts of gold and 1 of copper; the silver coinage alloy of $\frac{9}{10}$ of silver and $\frac{1}{10}$ of copper; and the bronze coinage alloy of 95 parts of copper, 4 parts of tin, and 1 part of zinc.—TR.

† According to the most recent investigation the word "bronze" is a contraction derived from *æs Brundusinum*—that is, metal from Brundusium (the modern Brindisi); just as *æs Cyprium*, metal from Cyprus, is the origin of the word "copper."

made of cast steel a generation ago, it has an impressive word to say in determining the fates of the peoples. Most lengthy investigations have been conducted by different states all over the world with regard to the bronze alloys, in the hope of finding the absolutely best alloy for casting cannon, and the books that contain accounts of all that can be said or thought about the bronzes would fill a library. The remarkable ease with which bronze can be cast makes it a most suitable material for producing works of art; and the great equestrian statues, for instance, show how safely it can be manipulated for such purposes.

Such works of art do not suffer hurt by long exposure in the open air, but they take on that beautiful rich rust which is called *patina*.* It is characteristic of patina that along with its malachite-green colour it has a metallic character; the peculiar metallic lustre appears through the colour. In this respect it is entirely different from any colouring material; for if a statue is made lustrous by a coat of varnish, for instance, the gloss is altogether superficial and does not come from within.

Copper alloys with zinc just as readily as with tin. There is a great demand for *brass*, which is the product of mixing copper and zinc. Although zinc was not isolated until the eighteenth century (see p. 282), yet the observation had been made long before that the metal obtained by smelting copper ores was yellow, and not red, when certain other ores were added before smelting; these other ores were called *cadmia* by the ancients, and at a later time the name

* If much coal is burnt near to bronze statues the sulphurous acid that is sent into the air along with the soot, which in itself is hurtful, so greatly retards the formation of patina that in many cases none gets formed.

calamine was given to them. We know now that the substances called *cadmia* or *calamine* were ores of zinc. Aristotle, about 330 B.C., tells that a kind of copper was found in India which could be distinguished from gold only by its taste; for whereas it was very pleasant to drink out of golden vessels, all vessels that contained copper had a disagreeable metallic taste. Aristotle recommended this means of distinguishing the two metals as an analytical method very suitable for the time.*

Brass can be made to resemble gold very closely by using suitable quantities of the constituent metals; and various articles made of this alloy, which is known as *tombac*, came into the market. The addition of some lead produces a colour which very closely resembles that of gold, but the product is not very lasting, as it soon oxidises in the air. By covering this alloy, or tombac, with a little gold the substance known as *talmi gold* is produced.

We should not pass over "*cuivre poli*," although that substance is going out of fashion. It is something between brass and bronze, and may be described either as a bronze rich in zinc or a brass poor in tin; it is nearly as cheap as brass—at present the cost of zinc is something less than an eighth of that of tin.

Nickel silver is produced by melting together copper, zinc, and nickel. This alloy played an important part from 1820 until about 1860; but it has been driven into the background

* He also relates that the Mesynœcians, a people living towards the north, made copper yellow by melting it with a certain earth, which must have been an ore of zinc. Some would derive the [German] word *messing* [= brass] from the name of that people; others say it comes from *möschen* or *maischen*, an older form of *mischen* [to mix]; and the brothers Grimm derive it from *massa*, a word used in the Middle Ages to express an unworked lump of metal.

by the introduction of silver electro-plated goods. It was at first customary to strongly plate goods made of nickel silver. Cheaper white metallic mixtures were, however, soon introduced as the material to be plated—for instance, *Britannia metal*, which is produced by melting together 90 parts of tin and 10 parts of antimony ; but this in turn has been replaced by yet cheaper materials.

In conclusion, we must mention *type metal*, which is an alloy that we certainly do not often have an opportunity of seeing, although it serves to multiply our intellectual and spiritual nourishment. Lead is the chief constituent of this alloy ; and to this are added antimony and a little tin and other similar metals. It is unfortunate that no one should have been able to produce an alloy suitable for use in printing without putting lead into it, because if this were done a final stop would be put to the serious cases of chronic lead poisoning which are not uncommon among compositors.

We have now seen what new valuable properties can be given to such very useful metals as copper, zinc, and others by alloying them. Iron, which we considered in great detail, is an exception in this respect. All the efforts made to improve the properties of iron by mixing it with other metals were without result until the year 1895. But success certainly seems to have come at last, especially in increasing the hardness of steel by mixing it with a little nickel, in accordance with results which were obtained in some of the French works ; the hardness of the best steel is to that of *nickel steel* as 4 is to 7. Very durable gun barrels of heavy calibre, and also torpedo boats, have been manufactured of late years of nickel steel, and it has also been used for making armour plate for men of war, notwithstanding its high price. Nickel steel does not rust in sea-water ; moreover, the bottoms

of vessels made of this alloy do not become foul by the growth of crustacea and sea-weed, so that the costly and tedious process of docking the vessels for cleaning is almost unnecessary.

The invention of nickel steel has made possible the production of steam turbines, so much spoken of nowadays. These turbines require to be furnished with blades of 2 or 3 metres (say 2 or 3 yards) diameter, making 4,000 revolutions per minute. The centrifugal force under these conditions would tear pig iron to pieces like paper-sheets; but the hardness of nickel steel is so great that blades of that material can bear four or five times this strain. On account of its hardness and resistance to disintegration, nickel steel is also used in making parts of motor-cars. In this connection steels are used which were not even thought of a few years ago. The high price of these steels is of no importance compared with their durability and the possibility of making with them very small explosion machines. Such steels can be made only at the very high temperature of the electric furnace. The best of the electric furnaces for melting steel is that introduced by Girod. The principle of this furnace is made clear by the figure (24). The melted metal, M, is placed in a fire-resisting vessel, P; the metal is covered with a layer of molten slag, S; by the two fixed metallic contact pieces, C, the current passes into the metal, which is made one of the electrodes, and to the other carbon electrode, A. The electric furnace makes possible the production on a large scale of steel as valuable

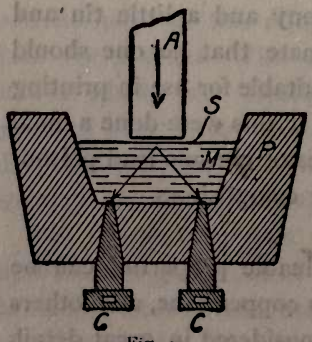


Fig. 24.

as crucible steel (see p. 271); the soft iron produced in Bessemer converters, or in Martin furnaces, can be refined in the electric furnace at a very high temperature without exposing it to the action of gases produced by the combustion of coal or coke. Addition of chromium, vanadium, titanium, silicon, etc., can be made to the steel in the electric furnace, for the purpose of producing steel having special properties which fit it for special uses.

We have mentioned the names of some rare metals. In recent years the names of several other rare metals have come to be often in men's mouths. Electric lighting has made people accustomed to hear of tantalum, tungsten, and osram lamps. When Edison introduced electric glow lamps he used very fine filaments of carbon as the material which was raised to so high a temperature by the electric current that it became luminous. It was necessary to remove the air completely from around the carbon filament, else the carbon would have been burned to carbonic acid ; the filament was suspended in a glass globe from which all the air had been removed. The light-giving capacity of such a carbon filament is very unfavourably related to the quantity of electricity which passes through it. Attempts were made to find filaments better suited for their purpose than those of carbon; after working for twenty-five years the distinguished technologist succeeded. At first he used thin wires of metal in place of the carbon filaments. The metals used in ordinary life, such as iron, copper, etc., melt when they are heated by electricity, in a space free from air, until they glow. It was necessary to find metals the melting points of which are so high that they do not melt under these conditions. Investigations were made of metals the ores of which occur only in relatively small quantities, metals which had been

used only by chemists in their laboratories for purely scientific purposes. These metals were produced in larger quantities for the first time in electrical factories, and their behaviour was studied when in the form of fine threads. Many difficulties had to be overcome before fine threads could be made of metals which melt only at very high temperatures, and are exceedingly hard to work. A fine thread of tantalum glows in the tantalum lamp, of tungsten in the tungsten lamp, and so on. The advantage possessed by these lamps is that they emit at least twice as much light as the old Edison carbon filament lamps when the same quantity of electricity is passed through them as through carbon lamps; in other words, they give as much light as the older lamps at half, or less than half, the cost.

Everything that has been brought forward in these lectures up till now has been concerned with knowledge which either is for, or can be applied to, the advantage of mankind in general. We picture mankind to ourselves as a whole constantly striving to advance, but restricted by the conditions of the time. But chemistry has also for long sought to place its results at the service of the individual who comes, lives, and departs, and who during the short space of his life is too often subject to sickness and laid low by illness.

An older period in the history of chemistry is distinguished as the time of the *iatro*, or medical, chemists. But the advances made in this direction, as in so many others, since the year 1803 put into the shade all that had gone before.

The first step in this direction was the discovery of the *alkaloids*, which is the name given to certain substances of an alkaline character that are present in plants. It was

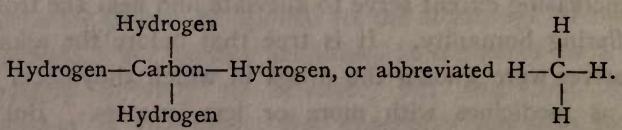
supposed until that discovery was made that only acids, such as tartaric and citric acid and the like, and neutral substances, such as sugar and starch, could be obtained from the vegetable kingdom. But in investigating certain medically active drugs in 1803, Derosne discovered a substance with an alkaline reaction to which he gave the name of *opium salt*. This result struck him as so remarkable that he speaks of the salt as a "*matière végéto-animale toute particulière*." It was not until 1817 that pure *morphine*, an impure form of which constituted the opium salt of Derosne, was prepared and was finally proved to be a vegetable substance capable of combining with acids after the manner of a true base.

We need not now enter into details concerning the value of such an alkaloid as *quinine* as a febrifuge, or of *morphine* as a sleep-giver, or of *atropine* for opening the pupil of the eye, or of *cocaine* as a local anæsthetic or a kind of chloroform active only at one spot, or of similar alkaloids which to an ever increasing extent serve to alleviate and heal the troubles of suffering humanity. It is true that before the alkaloids themselves were known the drugs in which they occur were used as medicines with more or less success. But the alkaloids are often mixed in these drugs with so many other substances which modify their especial activity that the action of the alkaloid may sometimes be almost entirely suppressed. This is the case, for instance, with morphine, as compared with opium taken directly from the plant, and from which morphine is extracted. The action of opium as a whole makes it useful for certain purposes, but not for employment as a sleep-producer. One kilo. of morphine costs about 360 marks ; 1 kilo. of opium about 25 marks [1 lb. of morphine costs about £8 ; 1 lb. of opium about 10*s*.].

The chemical investigation of alkaloids shows, as we might

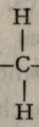
expect, that the atomic complexes of which they consist are very far from being simple. We have already learned (see pp. 22 and 66), that in order to have clear conceptions about a chemical compound it is not enough to know the number of atoms which build up the compound, but that we must also disentangle the atoms and discover how they are connected with one another. It is only when this problem has been solved—and even one who is not a chemist will understand how extraordinarily difficult such a problem may be—that attempts can be made in the laboratory to reverse the procedure, and that the task of building up artificially such an atomic complex from the single atoms—that is, of synthesising the natural product—can be entered upon.*

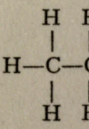
The hydrocarbon which is called methane or marsh-gas is composed of a single atom of carbon and four atoms of hydrogen—thus



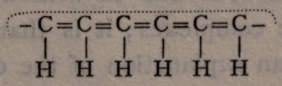
Now we know (p. 22) that organic compounds may be regarded as derived from this hydrocarbon by supposing that other atoms, or atomic complexes, are substituted for the hydrogen atoms of methane [or derivatives of methane], one monovalent residue taking the place of another such residue, or a divalent taking the place

* It is only about forty years since the problem of building up, from atoms of carbon, hydrogen, and oxygen, ordinary pure spirit, which is a comparatively simple substance—its composition being expressed (see p. 85) by the formula C_2H_6O—was solved in the laboratory. The alcohol that is made in the laboratory is, however, enormously more expensive than that which is obtained by fermentation.

of a divalent, or a trivalent the place of a trivalent residue. The group  , for instance, is a monovalent

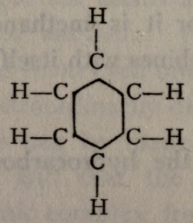
residue of methane, for it is methane *minus* one atom of hydrogen. If this combines with itself we have the molecule  , which is the hydrocarbon ethane, C_2H_6, which we have already become acquainted with (see p. 23).

We can think of these chains of carbon atoms as lengthened to any extent, by repeating the replacement of H by CH_3 (see p. 22), and also as branching out and even as returning upon themselves in the form of rings. Let there be a hydrocarbon consisting of a chain of six atoms of carbon to each of which only a single atom of hydrogen is linked (all the other linkings compensating each other as "double linkings," represented by double lines); we shall have the following:



Parts of the capacities for combination of the two carbon atoms at the ends of the chain are not satisfied; they hang in the air, so to speak. In 1866 Kekulé (who was then Professor of Chemistry at Bonn) made the memorable suggestion that the two carbon atoms at the ends of the chain are linked one to another; hence, if one regards the carbon atoms as symmetrically arranged, they are held

together in the form of a ring. As it is inconvenient always to draw circular figures, the custom has been adopted of drawing straight lines between the six carbon atoms, whereby the circle becomes a hexagon, a figure which is constantly met with in chemical literature.



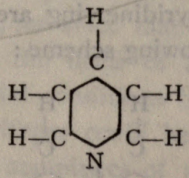
The hydrocarbon represented by the above scheme is the most simple imaginable under the conditions laid down. It is composed of six carbon atoms and six atoms of hydrogen; its formula is therefore C_6H_6. This hydrocarbon was discovered in 1826; the name *benzene* is given to it, from *benzoic acid*.

Benzene is found in considerable quantities in coal tar; it is the mother substance of an enormous number of compounds, among which may be mentioned the aniline colours. The aniline colour industry could not have attained the flourishing condition it is now in without the conception of ring-formed atomic complexes; it is that conception which has made possible an explanation of the chemical behaviour of the aniline compounds, and has led to advances in their investigation.*

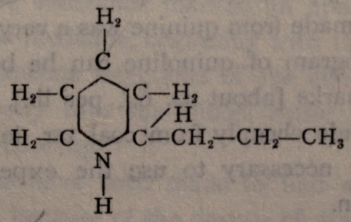
It has been known since the eighties of last century

* I have omitted about a couple of pages here, wherein the author speaks of the great advances made by German chemists in the syntheses of complex compounds, and quotes from Ostwald a passage in praise of the German methods of study as compared with those prevalent in England.—TR.

that ring-formed atomic complexes are constituted not only of atoms of carbon and hydrogen, but that the closing of the ring can be brought about by atoms of nitrogen also. Nitrogen is represented by the symbol N, and the simplest possible compound of this kind is C_5H_5N.



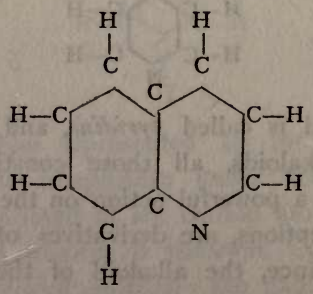
This compound is called *pyridine*, and is found in coal tar. All the alkaloids, all those constituents of plants which have such a powerful action on the human organism, with a few exceptions, are derivatives of this compound. *Coniine*, for instance, the alkaloid of the poisonous plant hemlock, the empirical formula of which is $C_8H_{17}N$, is represented by the following atomic arrangement:



The method of the arrangement of the atoms in this substance was made known fully by Ladenburg; and this atomic complex, which up to that time had been built up only by nature in plants, was prepared artificially from pyridine by him in 1888.

The investigation of *quinine*, $C_{20}H_{24}N_2O_2$, the most celebrated of all febrifuges, has been carried so far that, since

the year 1909, we know how the 48 atoms of this compound are arranged relatively to one another. Quinine is constructed in a much more complicated way than coniine, for example. But *quinoline* is easily obtained by splitting up quinine; and investigation has shown that quinoline is an atomic complex of two rings, and that in this compound a benzene ring and a pyridine ring are combined in the way represented by the following scheme :



As a kilogram of quinine still costs about 40 marks [about 18*s.* per lb.], although the price has fallen considerably, the quinoline made from quinine was a very expensive substance ; but a kilogram of quinoline can be bought to-day for less than 10 marks [about 4*s.* 6*d.* per lb.], because this alkaloid can be made cheaply from coal tar derivatives, so that it is no longer necessary to use the expensive quinine for its preparation.

As it was long known that quinoline is what one might call the skeleton of quinine, the question suggested itself whether it would be necessary to clothe this skeleton with exactly the same atoms and atomic complexes as are contained in quinine in order to produce a substance with the qualities of a febrifuge ; whether, if quinoline were transformed into an arrangement of atoms which, judging from the sum of our experience, would be suitable, the new

substance, although only roughly approximating to the natural product, would resemble that product in possessing the power of reducing the bodily temperature of feverish patients.

After many trials the first artificial febrifuge made its appearance in 1881, and to it was given the name *kairine*. This substance has been replaced by more active bodies, and has long been forgotten, for since that time one new remedy has followed hard on the heels of another. When some knowledge of the special conditions had once been gained, it was found that febrifuges could be prepared by putting together much simpler complexes of atoms than quinoline, and so it became easier to make such bodies in the laboratory.

The two substances which have proved to be the most practically useful are *antipyrin*, the atomic arrangement of which is very complicated, but which is not a derivative of quinoline, and *phenacetin*, a body with a comparatively simple arrangement of atoms.

We have already mentioned *morphine*, the introduction of which sleep-producing substance marked an epoch in the advance of therapeutical medicine, beginning with 1855, when Wood first used subcutaneous injections of the alkaloid, and so, by sending it directly into the blood, made its action quicker and more trustworthy.

Very many attempts have been made to find a suitable substitute for morphine because of the danger of that craving for it which is apt to follow the use of this drug. The first substitute was *chloral*, which, as its name suggests, bears some chemical relation to *chloroform*.

As time has gone on the number of these substitutes for morphine has become legion, for it has been found that substances of the most different kinds have this common property of producing sleep. Common alcohol is a sleep-

producer; but the use of it in quantity is apt to be followed by unpleasant effects on the next day; and it is the same with many of the drugs that have been introduced recently; they produce sleep, it is true, but they also produce many unpleasant effects. The number of those soporifics that are effective has diminished of late years; but there are still too many of these drugs in use.

While the special purpose of these sleep-producers is to induce a sleep which as closely as possible simulates natural sleep, it is also well known that there are substances which produce so deep an unconsciousness that the most severe operations can be performed without the patient feeling any pain.

The first substance to be employed for this purpose was *ether*, a body that is easily prepared from alcohol. As ether is more conveniently obtained by distilling alcohol with sulphuric acid, it used to be called, and is still popularly called, *sulphuric ether*, although it does not contain a trace of sulphur, a fact which has been known for about a hundred years.

Ether was discovered about 1530 by Valentinus Cordus, who was Professor of Medicine at Wittenberg; and as early as 1541 its sleep-producing properties were known to Theophrastus Paracelsus Bombastus. In one of his books * he says †: "This sulphur" (he means ether) "has an attraction for others; fowls take it and sleep for a time, waking again without any hurt." ‡

* Vol. i., p. 1064, of the complete reprinted works of Paracelsus, published at Strassburg in 1603.

† "Zum andern hatt dieser Sulphur eine Süsse, dass jhn die Hühner all essen, vnd aber endtschlaffen auff ein Zeit, ohn schaden wieder auffstohndt."

‡ In another part of the same book Paracelsus extols ether as a remedy in all complaints. Hoffman, a clinical physician of Halle, about 1750 strongly recommended a mixture of three parts spirit with one part ether as a soothing and pain-stilling drug, and the mixture became a popular remedy under the name of *Hoffman's drops*.

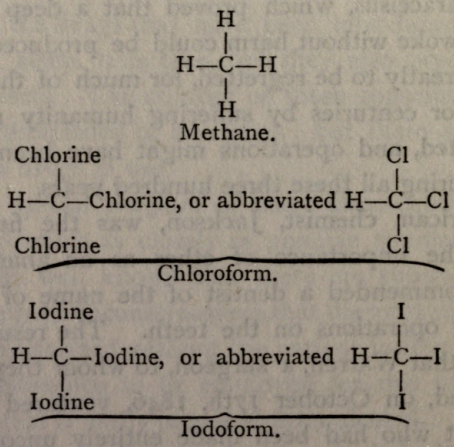
Three hundred years, unfortunately, passed before the full importance was appreciated of the experiment on animals made by Paracelsus, which proved that a deep sleep from which one awoke without harm could be produced by ether; and this is greatly to be regretted, for much of the pain that was borne for centuries by suffering humanity might have been alleviated, and operations might have been performed painlessly during all these three hundred years.

An American chemist, Jackson, was the first fully to appreciate the importance of ether as an anæsthetic; in 1846 he recommended a dentist of the name of Morton to use it during operations on the teeth. The results were so remarkable that Warren, a surgeon, to whom they had been communicated, on October 17th, 1846, ventured to operate on a patient who had been made entirely unconscious by ether. The painless performance of surgical operations dates from that day.

A search began at once to be made for specifics which should, if possible, be more suitable for bringing about the desired effect than the very explosive ether—the application of an actual cautery, for instance, was impossible when ether was employed; and as early as 1847 Simpson recommended chloroform, which has held the field, on the whole, since that time, although attempts have been constantly made to replace it by other and more efficient substances, or mixtures of substances.

Chloroform was prepared for the first time in 1831 by Liebig from chloral; it is manufactured to-day by the action of chloride of lime on alcohol. Chemically considered chloroform is a very simple substance. If three atoms of hydrogen in the hydro-carbon methane, with which we are now so familiar, are replaced by chlorine—and this can be

done directly in the laboratory—we have chloroform produced.



In the above formulæ *iodoform* is placed beneath chloroform, to which it is closely allied. The abbreviated termination *form* is derived from the name *formic acid*; for the chemical constitution of these compounds is related to that of this acid, which, like them, is a derivative of methane very closely related to the parent compound.

In associating iodoform with chloroform we have passed from the class of *narcotics* to that of *antiseptics*, which have added the equable and regular healing of wounds to the painlessness wherein chloroform has enveloped the operations of the surgeon.

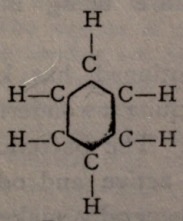
The world owes this improvement in the treatment of wounds, the greatest of its kind ever made, to Lister, whose genius was turned in this direction by the work of Pasteur on the lowest forms of living things.

When the bacteria which are present everywhere in the air get into wounds they cause suppuration, and they often also bring about other bad results which are extremely dangerous

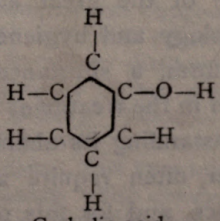
and sometimes fatal. As it is impossible to shut out the surrounding air from contact with a wound, care has been taken, since this method was introduced about the middle of 1870, to dress the wound with some substance capable of killing the bacteria in the surrounding air. *Carbolic acid* is the substance that Lister used for this purpose.

In well-appointed hospitals one goes a step further. Instead of trusting to antiseptics, the aseptic method is used ; that is to say, the instruments are boiled in order to kill bacteria, the overalls of the operator are sterilised in a current of steam, his hands are freed from bacteria by washing in alcohol, and the surfaces of the patient's skin are treated in a similar way, the bandages are made of sterilised wool, and so on. This treatment obviates contact of the patient with antiseptics, which are generally poisonous. It is, however only in the best appointed operating rooms of hospitals that this most modern surgical method can be used, because the number of preventive measures against bacteria, which must be paid attention to, is enormous.

Carbolic acid is closely related to benzene ; like that compound, it is obtained by distilling coal tar. Carbolic acid contains only one atom of oxygen in addition to the constituents of benzene, and has the following constitution :



Benzene.



Carbolic acid.

The great advance made by Lister will become more evident if we carry our thoughts back to the time of the

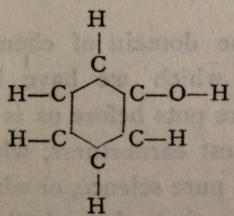
Franco-German war—that is, to the beginning of 1870. At that time the universal custom was, as it had been for centuries, to pick lint from old linen, without taking due precautions, and also without any suspicion of the enormous number of infectious substances that might be brought into the wounds by a material prepared in that way and not subjected to disinfection. It is certain that the use of such lint caused the death of many who would have been saved to-day. Lint is not used now, for it has been replaced by bandages that have been sterilised, and so made entirely free from bacteria. As everything that is allowed to touch a wound nowadays, including the hands of the operator, has been disinfected beforehand, most of the wounds heal without festering. Severe operations are of course still attended with danger, but what used to be the commonest source of danger, namely, fever following the wound, is as good as abolished. And there are many operations that are practicable since the discovery of the antiseptic treatment which would certainly have been followed in former times by suppuration leading to death.

There is nowadays an enormous number of antiseptics, and carbolic acid has very many competitors; at the same time the need and the demand for antiseptics keep increasing because of the great advances that are being made in bacteriology and hygiene.

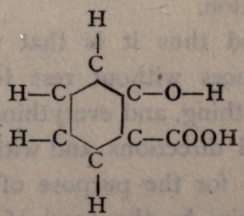
Iodoform, a substance already mentioned, has kept its position in the treatment of wounds in quite a wonderful way, notwithstanding its abominable odour. The bacteriologists, however, often require a much more active and odourless substance, and for this purpose they generally make use of *corrosive sublimate*, which, chemically considered, is *chloride of mercury*. An aqueous solution of this compound has the most powerful antiseptic action even when it is greatly

diluted; and were the compound not so extremely poisonous it would probably drive out almost all other antiseptics.

The public also require antiseptics which shall be quite odourless and tasteless, and not in the least poisonous, for making foods keep well, for instance. *Salicylic acid* is on the whole most favoured for this purpose. This acid was first obtained in 1839 from the bark of the willow (*salix*), and the name then given to it to recall its origin has been retained. The investigation of the arrangement of the atoms in this compound has shown that it is very closely related to carbolic acid, from which it can be prepared by replacing a certain one of the hydrogen atoms by the atomic complex COOH which is called *carboxyl*.*



Carbolic acid.



Salicylic acid.

* It should be remarked that chemical formulæ have been used in this book to express only the qualitative composition of compounds. Formulæ mean much more than this to chemists. They tell them the weight-relations between the elements which compose the compound formulated. The weights of the atoms of the individual elements, relatively to one another, are determinable and have been determined. These weights are referred to that of hydrogen, the lightest of the elements, the atomic weight of which is taken as unity. The atom of carbon, for example, is twelve times heavier, and the atom of oxygen is sixteen times heavier, than the atom of hydrogen. This knowledge makes possible the universal chemical sign-language, which demands no special linguistic knowledge, but is equally intelligible to the chemists of all nations. As Mack very rightly observes, the chemical sign-language, in its great simplicity and universal intelligibility, is comparable only with the notation of music.

The subject of chemical notation is treated more fully in the author's *Introduction to Modern Scientific Chemistry* (H. Grevel & Co., 1901).

Salicylic acid is now manufactured in large quantities from carbolic acid, which is obtained from coal tar, by a method that has gradually been brought to the greatest perfection. One kilo. of salicylic acid costs about $2\frac{1}{2}$ marks [about 1*s.* 4*d.* per lb.].

On the other hand, experience has shown that certain substances obtained from tar, which have very great antiseptic powers, can be used for all sorts of disinfecting purposes without being more than superficially purified, provided their other properties do not interfere with their use for these purposes. These substances can therefore be obtained at an extremely small cost, and by using them poorer people can themselves prevent many illnesses, and stop the spread of infection.

And thus it is that work in the domain of chemistry advances without rest in ways of which we have learnt something, and everything that nature puts before us is tried in all directions and with the greatest earnestness, whether it be for the purpose of advancing pure science, or whether the aim be the good of mankind or that of the individual man.

Here one must say—fermentation is classification. This book has had many important additions made to it since its first appearance sixteen years ago.

The criticism of Francis Bacon, Lord Verulam, is no longer applicable: "*Chymicorum autem genus ex paucis experimentis fornacis philosophiam constituerunt phantasticam et ad pauca spectantem*"; which may be freely rendered, "The craft of the chemists, from a few experiments made in the furnace, has constructed a philosophy which is fantastical and has regard to but a few phenomena." No longer, as in the olden days, is the whole covered with the mantle of alchemistic mystery, but it lies open before us. The attempt is, there-

fore, thoroughly justified to give, to him who stands outside, a glimpse into this world of keen intellectual activity, which should increase his general intelligence and quicken the special direction of his thought. As this book has been translated into all the chief languages, the author believes that the method he has adopted for diffusing general chemical knowledge will be found not unsuitable for his purpose.

INDEX

Abraum salz, 46
Acetic acid, 116, 119
Acetone, 119, 129
Acetylene, 35
Acid carbonate of ammonia, 187
Acid carbonate of soda, 187
Acid sulphite of lime, 172
Acids, 49
Air, composition of, 8 ; constituents of, 7, 27, 47 ; pressure of, 5, 75 ; weight of, 3
Albumen, coagulation of, 56 ; in various foods, 89 ; use of, in photography, 226
Albuminoids, 56, 57, 61, 90
Alchemy, 245
Alcohol, 85, 103 ; as a food, 115 ; quantity in beer, 102 ; in wine, 95 ; in spirits, 107, 114
Alcohol, absolute, 111
Alizarin, 156
Alkali, 49, 177
Alkaline pyrogallate in photography, 228
Alkaloids, 294
Alloys, 287
Alum, 140, 149 ; use of, in dyeing, 149 ; in tanning, 140
Alumina, 141, 142, 283
Aluminium, 282, 285
Amalgams, 204
Amber, 159
Ammonia, 29, 49
Ammonia soda process, 187
Ammonia water, 29
Ampère, 23 *note*
Amylic alcohol, 109
Anæsthetics, 302
Aniline black, 162
Aniline colours, 153, 298
Animal charcoal, 42
Anode, 235
Anthracene, 153
Antichlor, 146, 167
Antipyrin, 301
Antiseptics, 304
Aqua fortis, 181
Argon, 8
Aroma of wines, 95
Arrac, 114
Arrowroot, 67
Artificial butter, 65
Artificial fodder, 60
Artificial gems, 207
Artificial horsehair, 135
Artificial leather, 131
Artificial silk, 134
Artificial wool, 133
Ash analysis, 37
Atom, 24
Atomic weights, 307 *note*
Atropine, 295

Bacon and peas, 92
Baking, 84
Baking powder, 87
Barilla, 178, 185
Barley, 100

Barometer, 5
Base metals, 241, 252
Bases, 49
Beefsteak, 81
Beer, 99, 102
Beetroot sugar, 73
Benzene, 298
Bessemer steel, 271
Beverages, 77, 93
Bicarbonate of ammonia, 187 ; of soda, 187
Bichromate of potash, 232
Bimetallism, 243
Biscuit porcelain, 219
Blast furnace, 258, 260 *note*, 263
Blasting gelatin, 129
Bleaching, 144, 167
Bleaching powder, 145, 167
Blendes, 241 *note*
Blueing washed linen, 144
Body, maintenance of temperature of, 11, 91
Boilers, 108, 173, 267
Boiling under increased pressure, 108 ; under reduced pressure, 75
Bonbon making, 71
Bones, 41 ; fat of, 41, 193
Boric acid, 202
Bran, 68
Brandy, 114
Brass, 289
Brazilwood, 157
Bread, 86
Bread, black, 92
Breath, expired, 10
Breathing, 1, 11
Bricks, 209
Britannia metal, 291
Bromide of ammonium, 229
Bromide of silver, 222, 229
Bromine, 46
Bronze, 288
Bunsen's burners, 33
Butter, 65 ; artificial, 65

CALAMINE, 290
Calcined soda, 186
Calcining, 42, 186, 188
Calcium carbide, 35, 51
Calcium nitride, 51
Calcium oxide, 177
Calico printing, 158
Camera obscura, 224
Camphor, 103 *note*
Candle light, 17, 18
Candles, snuffing of, 19
Cane sugar, 72
Carbohydrates, 56, 64
Carbolic acid, 128, 153, 305
Carbon, 11, 16, 21, 91, 252
Carbon, bisulphide of, 30
Carbon monoxide, 252, 260 *note*
Carbonic acid, 12, 32, 85, 126, 187
Carbonic acid in beer, 102
Carbonic acid in expired breath, 10
"Carbonising," 134
Casein, 57
Cast glass, 204
Cast iron, 253, 258, 260, 261
Cast steel, 270
Catechu, 139
Caustic lime, 177, 207
Caustic potash, 177, 191
Caustic soda, 191
Cellite, 131
Celluloid, 131
Cellulose, 69, 125, 169, 171
Cementation steel, 269
Cements, 211
Cerotic acid, 20
Chalk, 176, 188, 191, 202
Chamois leather, 141
Champagne, 96
Charcoal, 16, 107
Chemical formulæ, 23, 130, 307 *note*
Chemistry, differences between, and physics, 1, 2
Chili saltpetre, 49, 50
Chloral, 301
Chlorate explosives, 130
Chlorate of potash, 130
Chloride of ammonium, 189
Chloride of calcium, 146, 189
Chloride of lime, 145, 184

Chloride of silver, 222
Chlorine, 145, 184, 189
Chloroform, 301, 303
Chlorophyll-grains, 36, 67
Chromegelatin, 232
Chrome leather, 142
Chrome yellow, 160
Chromium oxide, 142, 150, 220
Cider, 96
Circulation of the blood, 11
Clay, 209; modelling in, 212
Coagulation of albumen, 56; of blood, 59; of milk, 57
Coal gas, 28
Coal tar, 29, 153; colours, 153, 157
Cobalt, 160; chloride of, 163; oxide of, 220
Cocaine, 295
Cochineal, 151
Cocoanut butter, 195; oil, 195
Coffee, 77, 138
Coinage, 287
Coke, 29, 262
Collodion, 128; use of, in photography, 227
Colophony resin, 196
Colour photography, 234
Combustion, 7, 11
Common salt, 179, 187, 194, 214
Condiments, 77
Congo red, 152
Coniine, 299
Cooking, 77, 78
Cooking by gas, 33
Copal, 162
Copper, 281, 289; chloride of, 163
Copying ink, 163
Cordite, 130
Corrosive sublimate, 306
Cotton, 144
Cotton, dyeing of, 148, 150, 152
Cotton-seed oil, 65, 161
Cream, 57, 91
Crops, productiveness of, 52; rotation of, 38
Crucible steel, 271
Cryolite, 209
Crystallisation, water of, 186
Cuivre poli, 290

DAGUERREOTYPES, 225
"Degras," 143
Denaturalised spirit, 112
Dephosphorising iron, 273
Developers, 225, 227
Dextrin, 71
Diabetic patients, diet of, 70 *note*, 76, 90, 95
Diastase, 100, 105
Diazo compounds, 152
Diffusion, 9
Digestion, 53, 60
Dioxyanthraquinone, 156
Diphtheria serum, 59
Disinfection, 305
Distillation, 25, 102 *note*, 110
Distillation, dry, 28
Dough, 84
Drinks, spirituous, 85, 93
Dry plates (photographic), 229
Ducat, origin of word, 247
Dyeing, 147
Dyeing extracts, 157
Dynamite, 127

EARTH, infusorial, 127
Eau de Javelle, 146
Effervescing wines, 96
Eggs, 91 *note*
Electric furnace, 25, 292
Electric lamps, 293
Electro-deposition of metals, 284
Electrolysis, 285
Elements, 21
Emanation of radium, 239
Eosin, 163
Esparto grass, 169
Ethane, 23, 297
Ether, 302
Evaporation under reduced pressure, 75
Excise duties on spirits, 112

Fallow, 39
Fats, 19, 64, 192
Fatty acids, 20, 192
Fayence, 215
Felspar, 217
Felting cloth, 132
Felting paper pulp, 165, 168
Fermentation, 85, 93, 96, 101
Fermented liquors, 93
Ferrous sulphate, 227
Fibres, animal and vegetable, 132
Fibrin, 53
Fir wood, 173
Fire-clay, 212
Fireworks, 131
Fitted soap, 195
Flame, nature of, 17, 33
Florin, origin of word, 247
Flowers, manuring of, 41 *note*
Fluorescence, 236
Fodder, 60
Foods, 56, 63, 76, 89
Forging iron, 253
Fruit ethers, 95, 113
Fruits, fermentation of, 94
Fruits, ripening of, 69
Fuchsin, 148, 163
Fulling cloth, 132
Fulminating mercury, 125
Furriery, 141
Fusel oil, 109

Galena, 213
Gallotannate of iron, 162
Galls, 162
Gambier, 139
Garden manure, 41 *note*
Gas, 28
Gas, cooking by, 33
Gas generators, 277
Gas-lights, incandescent, 34
Geissler tubes, 235
Gelatin, 61
Gelatin emulsion process, 229
Gems, artificial, 207
Glances, 241 *note*
Glass, 199, 200, 203, 207
Glass, colouring of, 207
Glauber's salt, 180, 186
Glazes, 213
Glove leather, 141
Glucose, 71, 85, 94
Glue, 61
Gluten, 84
Glycerin, 19, 161, 192
Gold, 220, 242; production of, 245
Gold purple, 207
Gold standard, 243, 245
Grape sugar, 66, 71
Greek fire, 121
Guano, 42
Guncotton, 125
Gunpowder, 123
Gypsum, 44, 170

Hard soap, 193, 194
Hartshorn, salts of, 87
Hartshorn, spirits of, 30
Helium, 8
Hides, 136
High-fermentation beer, 101
Hoffman's drops, 302 *note*
Honey, 98
Hops, 100
Hydraulic cements, 211
Hydrocarbons, 21, 296
Hydrochloric acid, 183, 184
Hydrochloric acid in the stomach, 53, 60
Hydrogen, 22
Hydrogen peroxide, 147
Hydroquinone, 227
Hyposulphite of soda, 146, 226

Iatro chemists, 294
Incandescent gas-lights, 34
Indelible ink, 221
Indigo, 154
Indulin black, 162
Ink, 162
Inorganic salts, 49
Iodide of silver, 222
Iodine, 51
Iodoform, 304

Iron, 53, 256 ; output of, in different countries, 255 *note*
Iron in foods, 80

KAIRINE, 301
Kaolin, 217
Kathode rays, 235
Kid-glove leather, 141
Koumiss, 98
Krypton, 8

LACTIC acid, 57, 85
Lactic fermentation, 57, 87, 98, 137
Lakes, 150
Lead glance, 241 *note*
Lead glass, 206
Lead glaze, 213, 214
Lead oxide, 161, 206
Lead soap, 198
Leaden chambers, 180
Leaden pipes 173
Leather, 136, 140, 141, 143
Leblanc soda process, 179
Lighting-gas, 33
Lime, 176, 177, 188, 197, 210
Lime-sandstone bricks, 211
Limestone, 176, 210
Linen, 144
Linoleic acid, 160
Linoleum, 162
Linseed oil, 160
Liqueurs, 113
Loading paper, 170
Loading soap, 194
Logwood, 157
Low-fermentation beer, 101
Lunar caustic, 221

MADDER, 155
Majolica, 216
Malt, 100
Manganese, 272 ; peroxide of, 184
Manures, 37 ; artificial, 44, 46, 48, 50, 51, 52
Margarine, 65
Marsh-gas, 23
Mashing process, 100
Matches, 13
Mead, 98
Meal, 68
Melinite, 128
Mercerised cotton-wool, 134
Mercury, 204 ; poisoning by, 205
Metals, 241, 252
Methane, 23
Methylated spirit, 112
Milk, curdling of, 57 ; fermentation of, 98 ; nourishing value of, 91
Milk glass, 208
Milk-sugar, 57, 94 *note*
Milling cloth, 132
Mirrors, 204
Mixed diet, 64, 90
Molasses, 76, 190
Molecule, 24
Mordants, 149, 151
Morphine, 295, 301
Mortars, 210
Mother-liquor, 51
Muffle furnace, 220
"Mungo," 134
Must, 94
Mustard, 77
Mycoderma aceti, 117
Myricyl alcohol, 20

NAPHTHALENE, 153
Narcotics, 295
Negatives (photographic), 224, 227
Neon, 8
Nickel coins, 288
Nickel silver, 290
Nickel, steel, 291
Nitragin, 49
Nitrate of potash, 130 ; of silver, 221 ; of soda, 50
Nitre, 50, 120
Nitric acid, 51, 181
Nitroacid, 125, 128
Nitrocellulose, 120, 127
Nitrogen, 7, 47 ; assimilation of, by plants, 47 ; gatherers of, 48
Nitroglycerin, 127
Nitrogroups, 125, 128

Noble metals, 241
Nourishment, absorption of, 53; means of, 89; quantities of, necessary, 90

Oak bark, 138
Oil cake, 60, 196
Oil colours, 160
Oil, lighting by, 21
Oil painting, 159
Oil tanning, 142
Oils becoming rancid, 161
Oils, drying, 160
Oleic acid, 19, 160
Oleomargarine, 65
Olive oil, 21, 160
Open flame furnaces, 280
Opium, 295
Ores, 241, 252
Orthochromatic photographic plates, 232
Osram lamps, 293
Oxidation, 7
Oxides, 7, 252
Oxygen, 7, 11; absorption of, by the blood, 9
Ozone, 27

Painting, 160
Palm oil, 196
Palmitic acid, 19
Paper, 164, 165, 169
Papyrus, 164
Paraffin, 20, 27; candles, 20, 27
Parchment, 143, 164
Parting acid, 181
Patents, 172
Patina, 289
Peat, 278
Pepper, 77
Pepsin, 53, 60
Peptones, 53, 60
Persil, 147
Perry, 96
Petroleum, 21, 25
Petroleum ether, 26
Phenacetin, 301
Phosphates made soluble, 43, 44
Phosphoric acid, 41, 43, 275
Phosphorite, 42
Phosphorus, 13, 273; red, 14, 15
Photography, 221
Photography in colours, 234
Physics and chemistry, relations between, 1, 2
Picric acid, 128
Pig iron, 253, 255, 258, 260, 261, 273
Pig suet, 19
Pigment printing, 232
Plant albumen, 59
Plant ashes, 37
Plants, food of, 36, 41 *note*
Plasters, 198
Plate glass, 204
Platinocyanide of barium, 236
Platinum, 242
Porcelain, 209, 216; painting of, 220
Potash, caustic, 177, 191
Potash salts, 178, 190
Potashes, 45, 178
Potassium, 284
Potassium cyanide, 243
Potato spirit, 107, 109
Potatoes, 68; boiling of, 88; growing of, for making sprits, 107
Potter's wheel, 213
Pottery, 209, 213
Powder, smokeless, 125, 130
Pressed yeast, 105
Prismatic powder, 124
Propane, 23
Proteïds, 60
Prussian blue, 149
Puddling, 265
Pyridine, 299; bases, 113 *note*
Pyrites, 182, 241 *note*
Pyrogallic acid, 227
Pyrolusite, 184

Quartz, 206
Quartz glass, 206
Quebracho wood, 139
Quinine, 295, 299
Quinoline, 300

Radio-active substances, 239
Radium, 239
Rags, 165
Rails, 267, 268
Railways, 268
Rape oil, 21
Rare metals, 293
Red rays, 231
Regenerative furnaces, 280
Regenerators, 279
Rennet, 58
Resins, 161, 196
Retouching (photographs), 231
Reverberatory furnace, 265
Roasting ores, 252
Rolling iron, 266
Röntgen rays, 234, 236
Roots, 73, 156
Rotation of crops, 38
Rubies, 208
Ruby glass, 207
Rum, 114
Rusting of iron, 7
Rye, 68, 91 ; growing of, for making spirits, 107

Saccharin, 76
Saccharomyces cerevisiæ, 94
Sack, 96 *note*
Safety-matches, 14
Sago, 67
Salammoniac, 188
Salicylic acid, 307
Salt, common, 179, 183, 193, 214
Salting soaps, 194
Saltpetre, 50, 120, 122, 181
Salts, 49
Sand, 200, 210, 212
Sapphires, 208
Sequin, origin of word, 247
Serum, 59
Shellac, 162
"Shoddy," 134
Silica, 199
Silicates, 200, 211
Silicic acid, 200
Silicon, 272 *note*
Silk, 132, 134
Silvalin, 174
Silver, 243
Silvering glass, 205
Sintering, 210
Size, 166
Sizing paper, 166
Slag, 212, 258
Slaked lime, 177, 207
Smalt, 160
Smokeless powder, 125, 130
Soap, hard, 193, 194 ; loaded, 194 ; soft, 193
Soaps, 191, 192, 194
Soda, 176, 179, 187 ; calcined, 186 ; caustic, 191
Soda cellulose, 171
Soda crystals, 180
Sodium, 285
Soft iron, 280 ; steel, 277, 280
Soup, nourishing value of, 83
Soxhlet's apparatus, 58
Spiegeleisen, 272
Spirits, 104, 111
Starch, 67, 88, 100, 105
Starch-sugar, 69
Stassfurt salt deposits, 46
Stearic acid, 19
Stearin candles, 20
Steel, 253, 269, 271, 277, 292
Sticking plaster, 198
Stoneware, 214
Strass, 207
Straw, 170
Sublimate, corrosive, 306
Substantive colours, 152
Suet, 19
Sugar, 69, 72, 73, 85, 95
Sugar refining, 74
Sulphate of ammonia, 50 ; of soda, 179, 202
Sulphide of soda, 137
Sulphite cellulose, 171, 173
Sulphite of lime, 171
Sulphobenzimide, 76
Sulphur, 172, 180 ; in coal gas, 30
Sulphur-matches, 13

Sulphuric acid, 31, 180, 181, 202 *note*
Sulphurous acid, 147, 172, 180, 246
Sumac, 139
Superphosphates, 44
Sweating skins, 137
Sympathetic inks, 163
Syntheses, 296

TALBOTYPES, 223
Tallow, 65
Tallow candles, 19
Talmi gold, 290
Tannin, 138, 151
Tanning extracts, 139
Tanning stuffs, 138
Tantalum lamps, 293
Tar, 28, 153; tar colours, 153
Taxing spirits, 112; sugar, 73
Tea, 138
Tetrazo bodies, 153
Thomas's phosphate meal, 45
Tin, 150; chloride of, 150; oxide of, 216
Tin composition, 150
Tinfoil, 204
Tombac, 290
Torpedoes, 126
Trypsin, 54
Tungsten lamps, 293
Turbines, 292
Turkey red, 152
Turpentine oil, 103 *note*
Tuyères, 260 *note*
Type metal, 291

ULTRA-VIOLET rays, 231
Uranium compounds, 239
Uranium oxide, 220
Urea, 56

VARNISHES, 161
Vaseline, 27
Veal cutlets, 81
Vegetarianism, 89
Vinasse, 109
Vinegar, 117; essence, 118
Violet rays, 231
Volt, 23 *note*

WARP, 132
Wash leather, 143
Water, 66; electrolysis of, 284
hard and soft, 198; of crystallisation, 186
Water glass, 199
Wax candles, 20
Welding iron, 254
Wheat, average yield of, 52
Wheaten bread, 84; meal, 68; starch, 67
White light, 231
White of egg, digestibility of, 53, 60
White tanning, 141
Window glass, 204
Wine vinegar, 117
Wines, 94
Woad, 154
Wood, 16, 169
Wood charcoal, 16
Wood, dry distillation of, 28, 119
Wood gas, 119
Wood spirit, 119
Wood vinegar, 119
Woof, 132
Wool, 132, 148
Wool washings, ashes of, 196
Wort, 100
Wrought iron, 253, 261, 264, 265, 266

XENON, 8

YEAST, 85, 86, 93, 105
Yolk of eggs, 141

ZINC, 282
Zinc blende, 241 *note*

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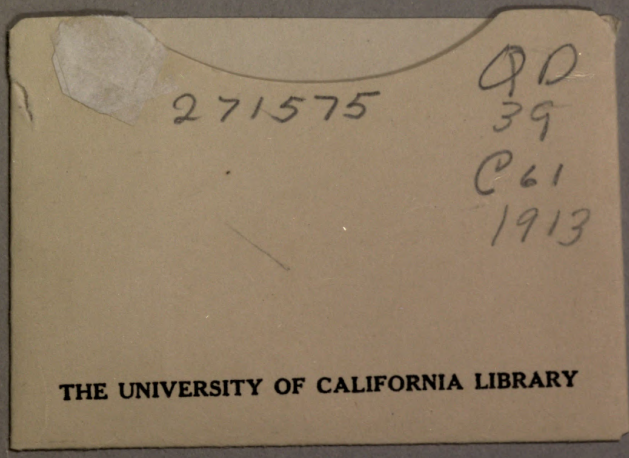
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